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Devolatilization and desulfurization of Iowa coal

Edmund Tao Kang Huang
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Devolatilization and desulfurization of Iowa coal

by

Edmund Tao Kang Huang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemical Engineering and Nuclear Engineering
Major: Chemical Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1977

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NOMENCLATURE

A	constant, dimensionless
a	constant, %
B	constant, K^{-1}
b	constant, K
E	effective activation energy, Kcal/mole
E_i	activation energy for species i Kcal/mole
f	the fraction of inorganic sulfur transformed into organic sulfur, dimensionless
G_1	the fraction of inorganic sulfur released as gases, dimensionless
G_2	the fraction of organic sulfur released as gases, dimensionless
ΔH	average decomposition energy, Kcal/mole
k	effective first order reaction rate constant, min^{-1}
k_i's	reaction rate constants
k_o	effective frequency factor, min^{-1}
k_i^o	frequency factor for species i, min^{-1}
m	heating rate, °C/min
n	reaction order, dimensionless
Q	constant, dimensionless
R	gas constant, 1.987 Kcal/mole-K
S_i	inorganic sulfur content in residue/100 gm raw coal, gm
S_i'	inorganic sulfur content in residue/100 gm deashed coal, gm

S_i^*	inorganic sulfur content/100 gm raw coal, gm
S_o	organic sulfur content in residue/100 gm raw coal, gm
S_o'	organic sulfur content in residue/100 gm deashed coal, gm
S_o^*	organic sulfur content/100 gm raw coal, gm
T	temperature, °C or K
T_o	room temperature, 20°C
t	time, min
t*	time required for complete conversion, min
V	volatile matter released at time t, %
V_i	species i released at time t, %
V_0	ultimate volatile matter released at temperature T, %
V_i^0	ultimate amount of species i released at temperature T, %
VM	volatile matter content by standard ASTM test, %
X	conversion, dimensionless
α	the ratio of the original inorganic sulfur contents of raw coal to deashed coal, dimensionless
β	the ratio of the original organic sulfur contents of raw coal to deashed coal, dimensionless

SCOPE

To face the increasing demand for energy with limited resources, man eventually has to explore the possibility of utilizing the relatively unlimited supply of solar energy or nuclear fusion. However, this is still beyond today's technology and requires a period of time for its development. In the meantime, the depletion of the oil and natural gas supplies demands an immediate energy substitute. Coal represents eighty percent of the proven recoverable fossil fuel reserves in the United States and is located over a vast stretch of land. It is therefore natural to infer that using coal is the solution.

However, the combustion of coal is not without problems. The main difficulty lies in the fact that most of United States coal contains a substantial amount of sulfur and, consequently, the gaseous sulfur dioxide emitted from power stations presents a serious air pollution problem. A majority of United States coal can not be burned directly without violating the Environmental Protection Agency regulations. The importance of evolving a process to overcome this problem in order to utilize the tremendous amount of coal reserve is obvious.

There are basically two approaches to the elimination of sulfur from coal. One approach involves the removal of

sulfur in the form of sulfur dioxide from the stack gas after combustion, while the other approach removes the sulfur from coal prior to combustion. The first approach can be divided into dry processes and wet processes depending upon whether a solid sulfur dioxide acceptor is injected during or after combustion, or a sulfur dioxide acceptor slurry is used to scrub the flue gas after combustion. The acceptors commonly used include limestone, dolomite, trimax clay, alkalized aluminum or magnesium oxide. There are many problems with this approach. For example, sulfur dioxide is of a stable form and has a rather low concentration in the stack gas and usually 4-5 times the stoichiometric amount of acceptor is needed to secure the desired elimination. The solid waste resulting from the process is difficult to regenerate and presents a serious waste disposal problem.

Most of the recent research effort is concentrated on the approach of cleaning coal before combustion. There are both mechanical and chemical processes used. The mechanical processes include conventional coal washing processes, magnetic separation, electrostatic separation and froth floatation. These only remove ash and some of the inorganic sulfur in coal.

For many United States coals that contain a large amount of organic sulfur and fine sized inorganic sulfur trapped within the coal matrix, chemical processes have to be employed

to achieve adequate sulfur elimination. Chemical processes can be categorized as coal conversion processes, bacterial treatment and chemical treatment of the coal. Coal conversion processes include coal liquefaction and gasification. These are usually operated either at high temperature or high pressure or both, and demand an extremely high operating capacity to be economically feasible. Bacterial treatment usually requires days of reaction with limited sulfur elimination. Further research is required before it can be of practical value. Chemical treatment of coal includes leaching and gas treatment. Leaching processes use chemical reagents such as nitric acid, hydrochloric acid, caustic solution or ferric solution to react with the sulfur compounds in coal and produce soluble sulfur compounds which can then be extracted out by some solvent. Research is being done on finding an inexpensive, recoverable reagent that can achieve adequate sulfur elimination.

Gas treatment is one of the chemical desulfurization processes for coal. It includes heating coal in a controlled atmosphere to convert the sulfur compounds in coal into volatile sulfur compounds such as hydrogen sulfide, sulfur dioxide or mercaptans. The gas treated product may have a reduced sulfur content and meet the requirements for a power plant fuel. However, two major difficulties remain to be solved before the process can be applied commercially: achieve

adequate sulfur elimination with a minimum amount of gas, and reduce the loss of heating value of the product. These require some knowledge of the desulfurization and devolatilization reactions under the particular treatment conditions.

Another reason to desulfurize coal by gas treatment is for metallurgical uses. It is highly desirable and frequently held essential that the sulfur content of coke in blast-furnaces be low to guarantee the quality of pig iron. Electrode coke also requires extremely low sulfur content. This desulfurization process is of importance to the eastern European countries, Russia and India because of their high sulfur content coal reserves. However, in view of the limited resources of low sulfur, high metallurgical quality coal, there is an increasing incentive to utilize high sulfur coal. The gas treatment process is gaining importance all over the world.

Iowa coal contains 5-9% sulfur, with about half being organic sulfur. Studies with the electron microscope have shown that a great portion of the inorganic sulfur (pyrite) is smaller than 10 μm and is trapped inside the coal matrix (Greer, 1975). These pyrite nodules, along with the organic sulfur, can not be removed by mechanical means. Therefore, some chemical process is required to achieve satisfactory sulfur elimination. Gas treatment is one of the options. In this dissertation, the devolatilization and desulfurization

reactions which are of major importance to the gas treatment process are investigated for Iowa coal.

DEVOLATILIZATION

Introduction

When coal is heated in an inert atmosphere, material known as volatile matter is lost from coal. Because of the complex nature of this process, a simple and adequate model of the reactions that occur during this process is not available. Some of the difficulties encountered in studying coal devolatilization are listed below.

1) Although the exact structure of coal is unknown, it appears to be made up of aromatic units containing various side chains cross-linked together. Devolatilization is actually the combined effect of simultaneous breaking of different bonds within the coal structure. Each decomposition reaction may have several consecutive steps. It is difficult to find a model which sufficiently describes these combined reactions with a single reaction parameter and covers a reasonably wide range of reaction conditions. On the other hand, to study the evolution of a specific gas, such as H_2, CO, CO_2 or CH_4 etc., will certainly shed some light on the understanding of the true mechanism of the reaction, but it does not show the whole picture of the process and it is difficult to apply the result from the study of a single species to predict the combined reactions.

2) There are always problems in bringing the sample to

the desired reaction temperature and in quenching the reaction after the experiment since there is volatile matter released during the heating and cooling periods. The amount of volatile matter released during these nonisothermal periods depends upon the rate of heating or cooling. It is also known that different heating rates lead to different devolatilization products (Peters and Bertling, 1965). This dependence on the conditions of the experiment results in further complications.

3) Depending on the size of the coal particle and the arrangement of the experimental apparatus physical processes such as heat transfer and the diffusion of volatile products out of the particle may affect the rate of the devolatilization reaction. This not only complicates the study, but limits the applicability of the reaction model developed from the data.

Early research concentrated on studying the rate of weight loss at a constant temperature condition. Some researchers investigated the evolution of one gas (Mullin and Berkowitz, 1968) or the devolatilization in a relatively small temperature range (Fitzgerald, 1956a; Den Hertog and Berkowitz, 1962) to simplify the study. Experimental techniques, such as dropping the sample rapidly into a constant temperature reactor (Shapatina et al., 1950; Wiser

et al., 1967) or heating the sample with a constant heating rate (Jüntgen and van Heek, 1968) were used to avoid the uncertainty during the heating period. Physical process limitations were eliminated by using small particles well dispersed or thinly spread in the reactor.

In the study reported here, a thermogravimetric method was employed to investigate the devolatilization of Iowa coal. The heating rate was controlled so the experiments were carried out under definite conditions. In order to alleviate physical process limitations, a small particle size and small quantity of coal were used, and the flow rate of carrier gas was kept high. Experiments were conducted under both constant temperature and nonisothermal conditions. The reaction kinetics and mechanism at different temperatures and reaction stages were studied and compared with the works of previous investigators. An attempt was also made to relate the results in the constant temperature process and constant heating rate process.

Review of Previous Work

Fundamental information and a detailed literature review on devolatilization can be found in the books of Van Krevelen and Schuyer (1957) and Lowry (1963). Jones (1964) and Yellow (1965) reviewed a number of devolatilization studies, most of which were done at low heating rates.

Recently, Anthony and Howard (1976) also made a thorough review on coal devolatilization, with a particular emphasis on rapid devolatilization. In this section only the literature closely related to the present study are reviewed.

Fitzgerald (1956a) and Van Krevelen et al. (1956) studied the devolatilization of bituminous coal in the plastic zone. They found that when coal was heated to between 350° and 500°C, it softened and showed a certain degree of fluidity. When measuring the fluidity of coal at 407°C, they noted that a maximum was reached at about 25 minutes, followed by a period of 80 to 90 minutes when the fluidity continuously declined. They attributed this effect to the formation and disappearance of meta-stable intermediates, and proposed the following reaction scheme:

$$\text{coal} \xrightarrow{k_1} \text{primary decomposition product + residue}$$

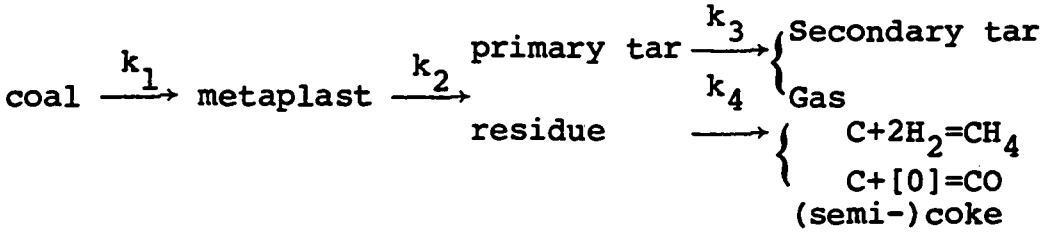
$$\text{primary decomposition product} \xrightarrow{k_2} \text{final decomposition product}$$

When $k_1 >> k_2$, the reaction followed first order kinetics. The rate equation they used was

$$\frac{dV}{dt} = k(V_0 - V) \quad .$$

In a later paper, Fitzgerald and Van Krevelen (1959) changed somewhat and extended their earlier reaction scheme to

cover the coke formation region.



Wiser et al. (1967) studied the pyrolysis of a Utah high volatile bituminous coal at temperatures ranging from 409°C to 497°C. They noted that there were three reaction regions, a second order region initially followed by a first order region and then a zero order region. In an attempt to explain this phenomenon, they proposed the following reaction scheme:

1. $Ⓜ\text{-}(CH_2)_x\text{-}Ⓝ\text{-}R \rightarrow Ⓜ\text{-} + \text{-}(CH_2)_x\text{-}Ⓝ\text{-}R$

2a. $R\text{-}Ⓟ\text{-}(CH_2)_yCH_3 \rightarrow R\text{-}Ⓟ\text{-}+\text{-}(CH_2)_yCH_3$

2b. $R\text{-}Ⓝ\text{-}(CH_2)_x \rightarrow R\text{-}Ⓝ\text{-}+(CH_2)_x$ where $x>1$

3a. $Ⓜ\text{-}+\text{-}(CH_2)_yCH_3 \rightarrow Ⓜ\text{-}(CH_2)_yCH_3$

3b. $Ⓜ\text{-}+\text{-}Ⓟ\text{-}R \rightarrow Ⓜ\text{-}Ⓟ\text{-}R$

Where Ⓜ, Ⓝ, Ⓟ are specific aromatic clusters within the coal matrix and R- is a segment of the coal "molecule".

This view of different reaction stages was also shared

by other investigators. Shapatina et al. (1950) analyzed the volatile products evolved during constant temperature pyrolysis of coal. They found that there was a rapid evolution of CO_2, H_2O, and CO in the initial period, followed by a somewhat slower and prolonged period of evolution of tar, gaseous hydrocarbon and hydrogen, and then further evolution of CO, CO_2 and H_2. Stone et al. (1954) also noted that the reaction order depended upon the degree of devolatilization and upon the temperature. In the initial period there was a rapid first order reaction, and the reaction became zero order in the final period.

All of the proposed reaction schemes consist of consecutive reaction steps with meta-stable intermediates, and the rate equation can be expressed in a general form

$$\frac{dV}{dt} = k(V_0-V)^n \ .$$

The temperature dependence of the reaction rate constant k is usually correlated by an Arrhenius expression

$$k = k_0 e^{\frac{-E}{RT}} \ .$$

Skylar et al. (1969) tried to use the above equations to fit nonisothermal devolatilization data for different coals and found that reaction orders from 2 to 8 were required. This cast much doubt on the validity of the equations.

Jüntgen and Van Heek (1968) used the nonisothermal kinetic method and successfully explained the release of ethane from a finely-ground coal at heating rates between $10^{-2} \sim 10^{5}$ °C/min. They commented that the release of methane or hydrogen was the result of more than one reaction and thus more complicated.

Some researchers considered physical processes to be the controlling mechanism of devolatilization. Berkowitz (1960) proposed that the decomposition of coal occurred rapidly in a short period and attributed the rate of weight loss to the pressure build up and the diffusion of gases through the coal pore controlling. The rate equation he used was

$$\frac{dV}{dt} = DP$$

where D was the effective diffusivity and P was the average gas pressure inside the coal pore. This rate equation also follows first order kinetics. Davies and Brown (1967) studied the thermal decomposition of a large spherical coal particle and proposed that the external heat transfer was the controlling mechanism. The rate equation they used was

$$\frac{dV}{dt} = \frac{hA(T_g - T_s)}{\lambda}$$

where h is the heat transfer coefficient; A, surface area; λ, heat of decomposition; T_g, the gas temperature; and T_s, the surface temperature of the particle. Peters (1960) used the following empirical equation to explain the zero order reaction observed for particles of 250 to 2,000 μm diameter:

$$\frac{dV}{dt} = 0.03\ (T_g - 330)/d^{0.26}$$

where d is the particle diameter. This result was interpreted as representing the propagation of the evaporation front ($T \sim 330°C$) through the particle, and the reaction rate was controlled by the overall temperature gradient. Koch et al. (1969) suggested that the reaction mechanism shifted from chemical reaction control to heat transfer control as the heating rate and the particle size of the coal sample increased.

If devolatilization of a coal particle is controlled by physical processes, the rate of reaction should depend on particle size. Badzioch and Hawksley (1970) and Howard and Essenhigh (1967) found no particle size influence for particles under 80 μm. Wiser et al. (1967) found no change on weight loss curves for samples of 60 to 74 μm vs. 246 to 417 μm. It appears that physical processes are important only when large particle sizes and fast heating rates are used, or when the physical arrangement of the equipment

hinders the release of volatile matter. In most cases chemical reaction is the controlling mechanism of devolatilization.

Experimental

Apparatus and material

The apparatus used in the experimental work was a Rigaku CN8001 H type thermal analyzer which included a thermal gravimetric analyzer (TGA) and differential thermal analyzer (DTA) unit, a temperature controlling unit and a data recording unit. There was a sample holder confined in a quartz reaction chamber of the TGA, DTA unit. The sample holder sat on a thermal balance which could detect a weight change of less than 0.1 mg. A chromel-alumel thermocouple was attached to the bottom of the sample holder to measure the temperature. There was another thermocouple to measure the temperature difference between the sample being tested and an inert reference sample (Al_2O_3). The temperature of the reaction chamber was regulated by a preprogrammable, high-power heater and a feedback type temperature controller. The heating rate could be varied from 0.25 °C/min to 160 °C/min and the final temperature of the reaction chamber could be controlled to $\pm$ 0.25 °C. During an experiment, the recording unit continuously plotted the weight, the rate of

weight change, the temperature of the sample and the temperature difference between the sample and inert reference sample. The schematic diagram of the system is shown in Figure 1. The detailed configuration of the sample holder unit is shown in Figure 2.

The coal used in the experiments came from the star mine, Mahaska county, Iowa, and was a high volatile C bituminous coal. The analyses of the the sample are listed in Table 1.

Table 1. Analysis of the coal sample

Proximate Analysis	As received
Moisture	0.88
Ash content	17.24
Volatile matter	41.11
Fixed carbon	40.77
Ultimate Analysis	
C	60.2
H	4.7
S	9.1
N	1.0
O	25.0
Calorific value (MJ/Kg)	27.2

Figure 1. Thermal analyzer system

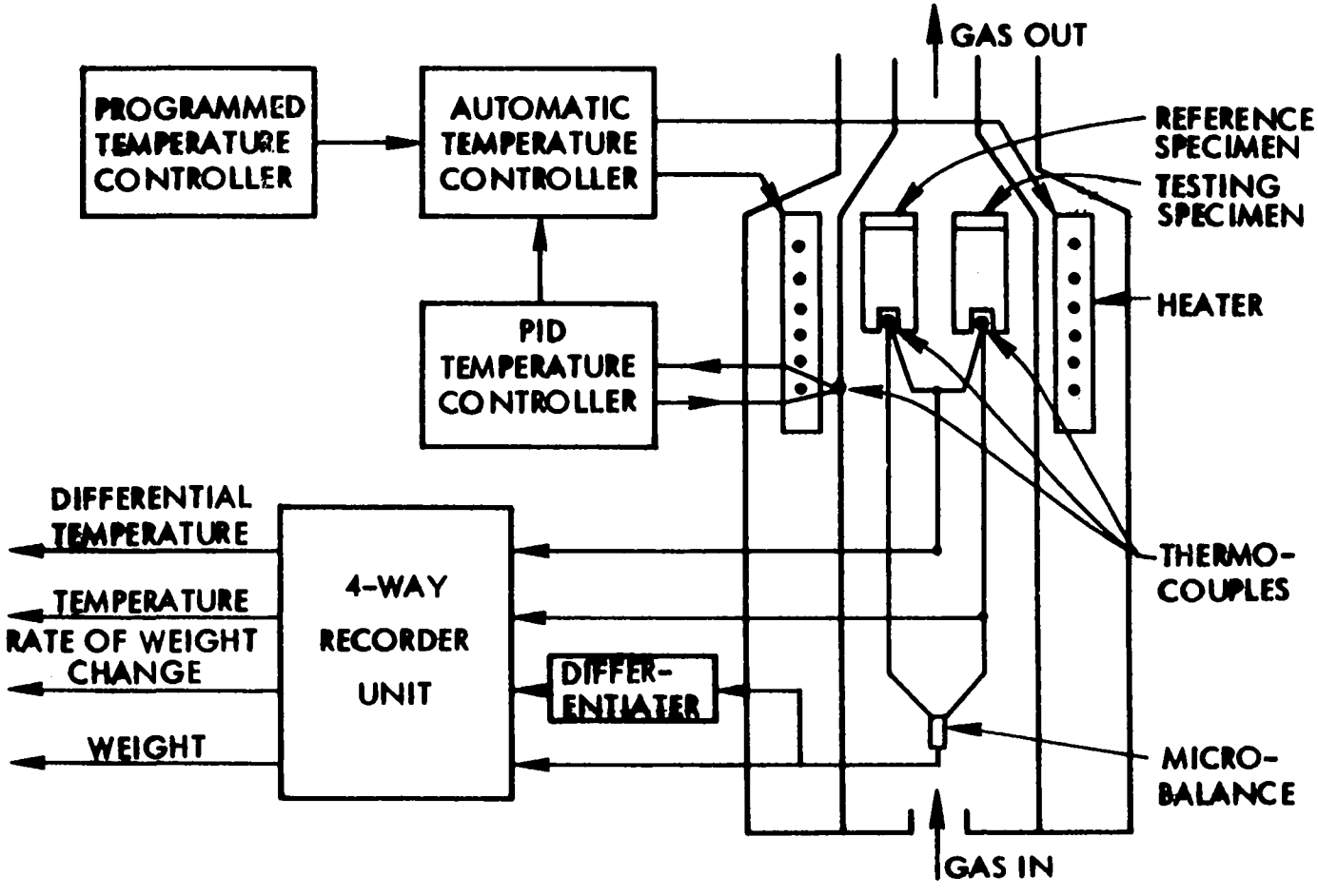
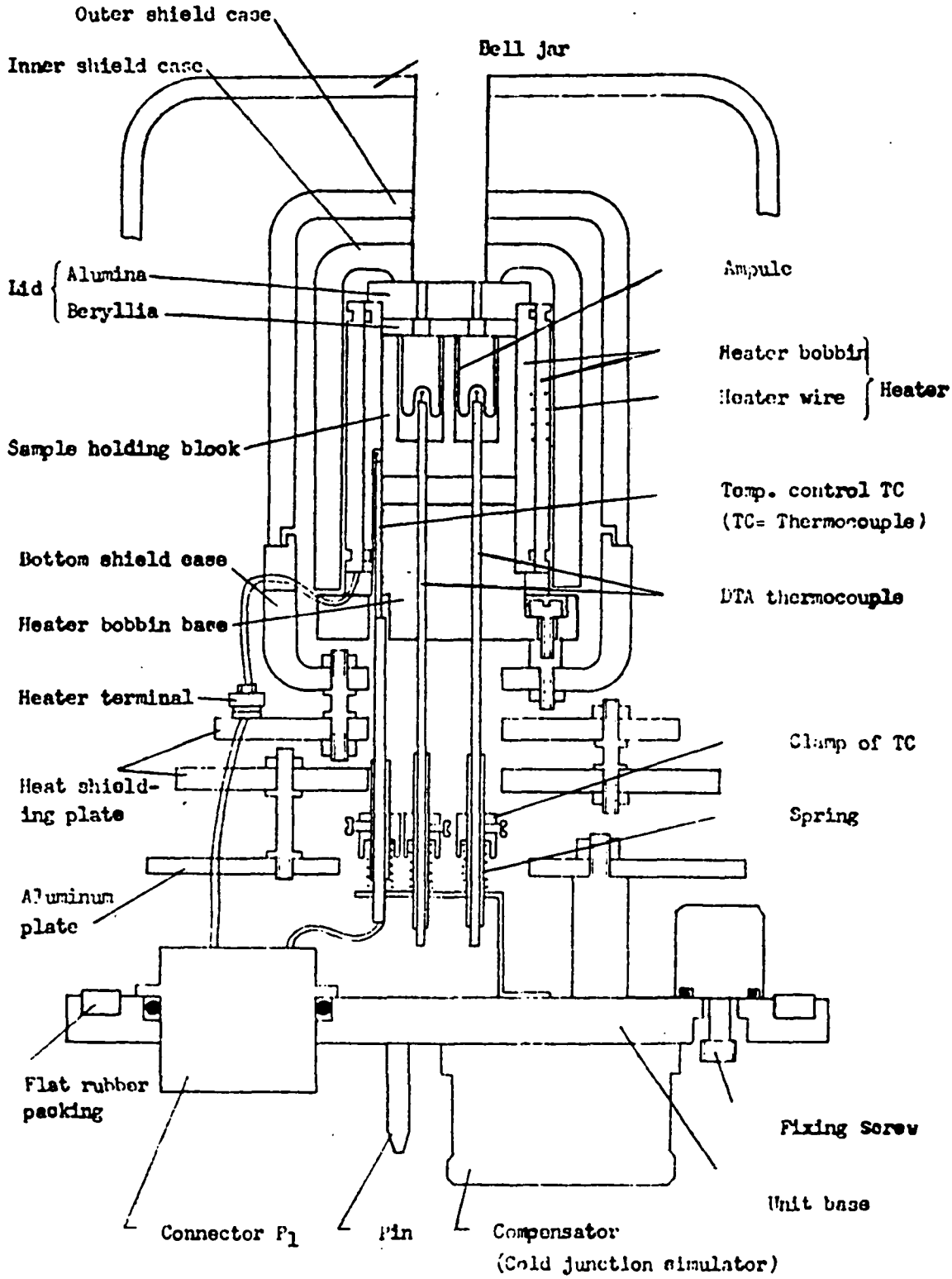

PROGRAMMED TEMPERATURE CONTROLLER
AUTOMATIC TEMPERATURE CONTROLLER
PID TEMPERATURE CONTROLLER
GAS OUT
REFERENCE SPECIMEN
TESTING SPECIMEN
HEATER
THERMO-COUPLES
MICRO-BALANCE
GAS IN
DIFFERENTIAL TEMPERATURE
TEMPERATURE
RATE OF WEIGHT CHANGE
WEIGHT
4-WAY RECORDER UNIT
DIFFER-ENTIATER

Figure 2. Sample holder unit


Outer shield case
Inner shield case
Bell jar
Lid
Alumina
Beryllia
Ampule
Heater bobbin
Heater wire
Heater
Sample holding block
Temp. control TC
(TC= Thermocouple)
Bottom shield case
DTA thermocouple
Heater bobbin base
Heater terminal
Clamp of TC
Heat shield-
ing plate
Spring
Aluminum
plate
Flat rubber
packing
Fixing Screw
Unit base
Connector P1
Pin
Compensator
(Cold junction simulator)

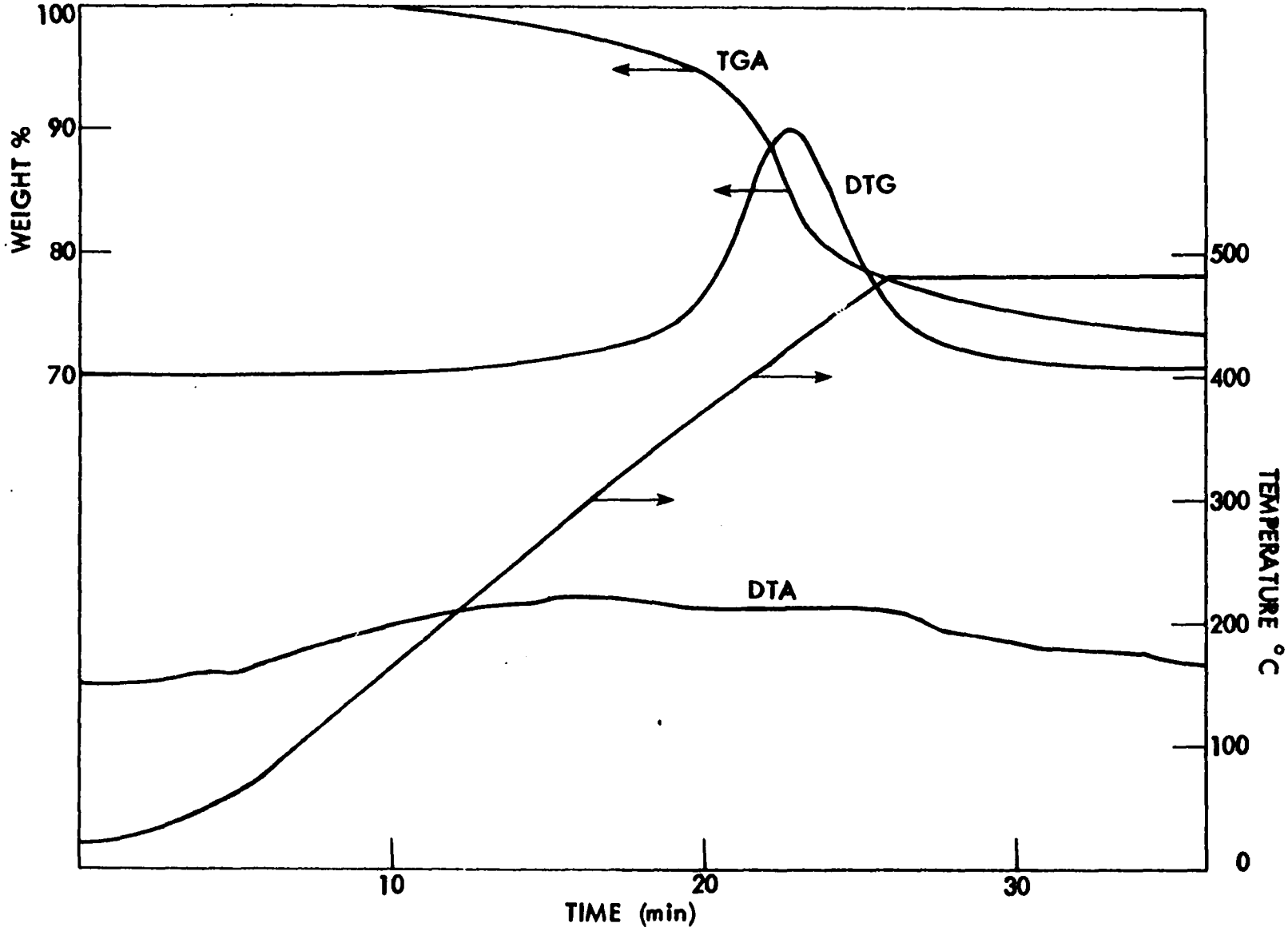
Procedure

In starting a run, approximately 25 mg. of the sample was ground to under 125 μm. After being dried in an oven at 110 °C for over 24 hours, it was placed in the sample holder inside the reaction chamber. Nitrogen was used as the carrier gas to sweep away the volatile matter evolved. The gas flow rate was controlled manually at a value of 0.08 liters/min. After choosing the heating rate, the heater and the recorder were turned on. The sample was then heated to the desired operating temperature and held at that temperature for the desired period of time. Meanwhile, the temperature, the weight, the rate of weight change and the temperature difference between the sample and reference sample were continuously plotted by the recorder. After the experiment, the heater was turned off. The reactor system was cooled to under 60 °C, and the solid residue was discharged from the sample holder. The above procedure were repeated for different experimental conditions.

Results and Discussion

A typical result from an experiment is illustrated in Figure 3. In this experiment the sample was heated with a constant heating rate of 20 °C/min to 480 °C and then

Figure 3. Typical thermal analysis result for Star coal in nitrogen


100
90
80
70
WEIGHT %
TGA
DTG
DTA
500
400
300
200
100
0
TEMPERATURE °C
10
20
30
TIME (min)

held at that temperature. The TGA curve represents the weight of the sample at various times, and the DTG curve shows the rate of weight change versus time. As shown in Figure 3, the devolatilization became appreciable at around 200 °C and reached the maximum rate of weight loss (peak of DTG curve) at about 450 °C. The DTA curve shows the temperature difference between the coal sample and an inert reference sample. As shown in the figure, the temperature of the coal sample is higher than the temperature of the reference sample. Thus, the reaction is exothermic.

Experiments were carried out for star coal over the range from room temperature to 750 °C and heating rates from 5 to 160 °C/min. Most experiments were conducted by using particles under 125 μm. In some cases a larger particle size (+250 μm - 500 μm) was used for comparison. The results are presented and discussed separately in three sections: ultimate weight loss at a given temperature, devolatilization at a constant temperature condition and devolatilization during constant rate heating.

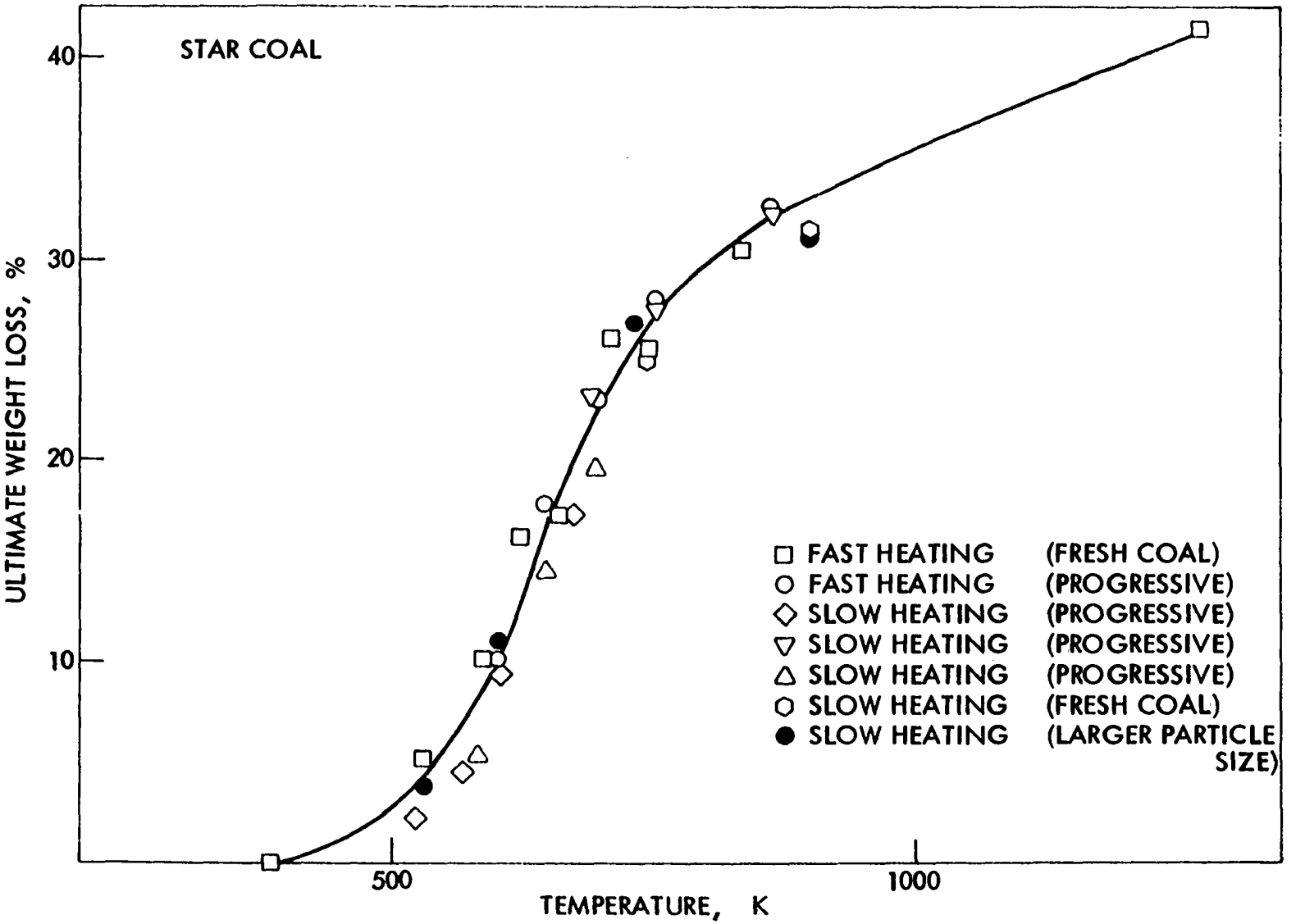
The ultimate weight loss at a given temperature

When coal is heated at constant temperature for a long period of time, the amount of volatile matter released will reach some limit. This limiting value of weight

loss is a function of temperature; the higher the temperature, the greater the weight loss. A series of experiments were made in which samples were heated to the desired temperature and then held there for about an hour until the change in weight became insignificant. The final weight loss was recorded as the ultimate weight loss of the coal sample at that temperature, V_0. Experiments were conducted using samples of different particle size and different heating rates were employed. Experiments also were carried out in which the coal was heated progressively or in steps to the final temperature. In these experiments, the coal was first heated to an intermediate temperature and held there for an hour. The temperature was then raised to some new value and the procedure repeated until the final temperature was reached.

The results for Star coal are shown in Figure 4. The ultimate weight loss follows an s-shaped curve as the temperature is increased with the sharpest rise occurring at around 650 K. Differences in particle size, heating rate and past temperature history of the sample did not have any significant effect on the total amount of volatile matter released. Some investigators (Badzioch and Hawksley, 1970; Chukhanov et al., 1962) have reported that a high heating rate gives rise to a higher yield of volatile matter. However, the heating rates they reported were in

Figure 4. Ultimate volatile matter released as a function temperature

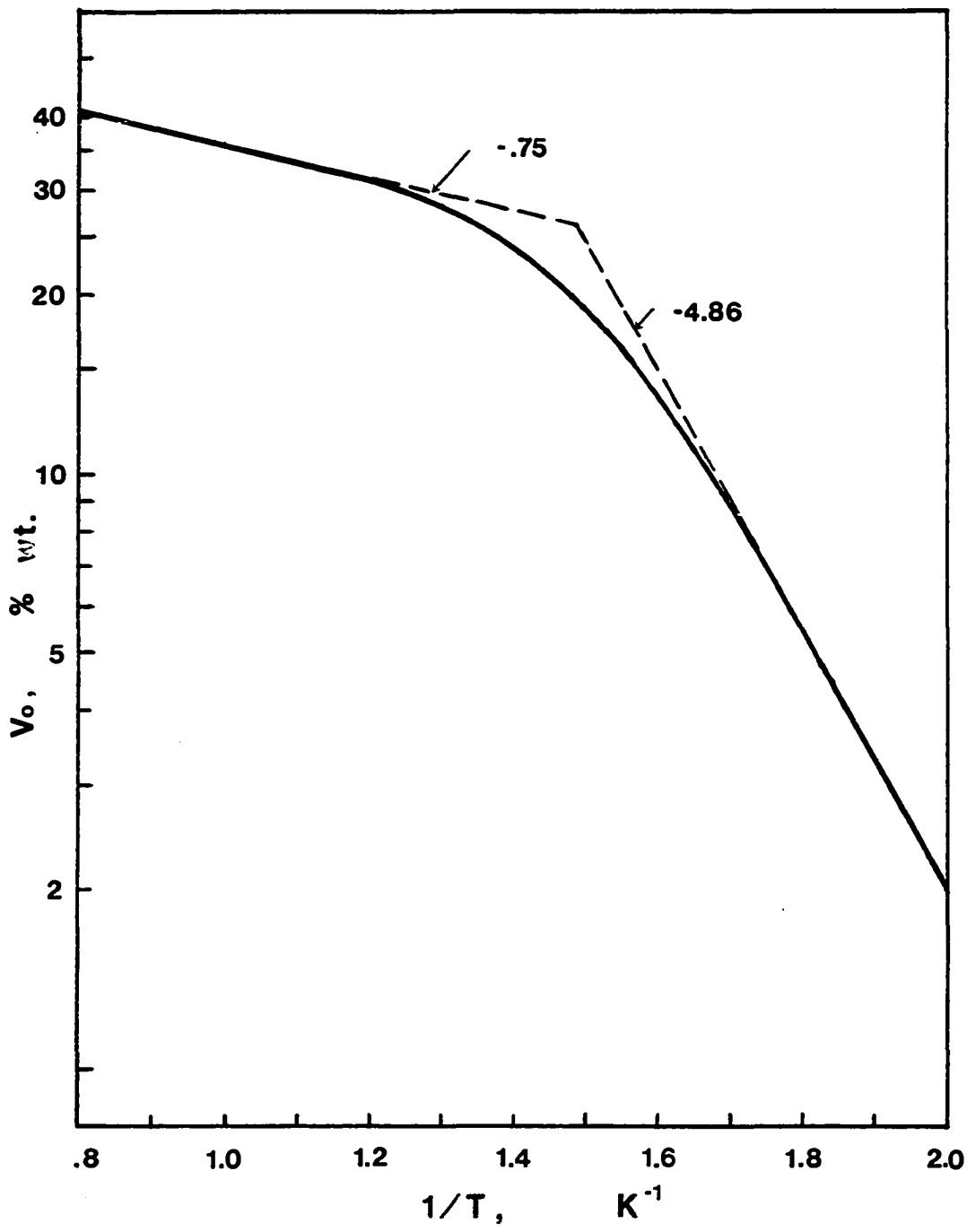

STAR COAL
ULTIMATE WEIGHT LOSS, %
40
30
20
10
500
1000
TEMPERATURE, K
FAST HEATING (FRESH COAL)
FAST HEATING (PROGRESSIVE)
SLOW HEATING (PROGRESSIVE)
SLOW HEATING (PROGRESSIVE)
SLOW HEATING (PROGRESSIVE)
SLOW HEATING (FRESH COAL)
SLOW HEATING (LARGER PARTICLE SIZE)

the range of 10^3 to 10^6 °C/sec, which is about three to six orders of magnitude higher than the heating rate employed in this experiment. It is possible that a different mechanism is responsible for the higher yield at such an extremely high heating rate. Under the conditions of this experiment it appears that the ultimate weight loss of Iowa coal is only a function of temperature.

The fact that the ultimate weight loss is independent of heating rate and past temperature history of the sample essentially rules out the possibility of competitive reactions as the mechanism of devolatilization and suggests that the reactive components in coal react independently. Competitive reactions going through different heating procedures would result in different product distributions and therefore different weight losses. This is consistent with the reaction mechanism proposed by Fitzgerald and Van Krevelen (1959).

The shape of the V_0 versus temperature curve has an inflection point at about 650 K. This is inconsistent with the model proposed by Badzioch and Hawksley (1970), $V_0 = VM[Q-A \exp(-BT)]$, and is closer to the Boltzmann type curve of $a\exp(-\frac{b}{T})$. The semi-logarithm plot of V_0 versus $\frac{1}{T}$ is shown in Figure 5. It is linear for temperatures below 630 K and above 750 K, with a transition stage occurring between these two temperatures. The low

Figure 5. Logarithm of ultimate volatile matter released versus 1/T


40
30
20
10
5
2
V_o, % wt.
-.75
-4.86
.8
1.0
1.2
1.4
1.6
1.8
2.0
1/T, K^{-1}

temperature asymptote has a slope of -4.86, while the slope of the high temperature asymptote is -0.75.

V_0 is the conversion limit at a given temperature and physically is the equilibrium conversion of the reaction. From the van't Hoff relationship,

$$\frac{d \ln V_0}{d(\frac{1}{T})} = - \frac{\Delta H}{R}$$

it can be seen that the slope of the ln V_0 versus $\frac{1}{T}$ curve may be viewed as an average decomposition energy. Since no single value of slope can be found in the temperature range studied, different components must be decomposing. In a paper by Fitzgerald and Van Krevelen (1959), it was reported that the original bonds in coal ruptured at temperatures between 570 and 770 K. This was termed the primary decomposition. At temperatures above 770 K the devolatilization reaction was dominated by the decomposition of the solid residue from the primary decomposition. This was termed the secondary decomposition. From Figure 5 the linear region at low temperatures spans the primary decomposition zone, while the linear region at high temperatures spans the secondary decomposition zone. It appears that the primary decomposition and secondary decomposition are the dominating reactions in their respective regions. The nonlinear region in between represents a transition zone between the two reactions. The average decomposition

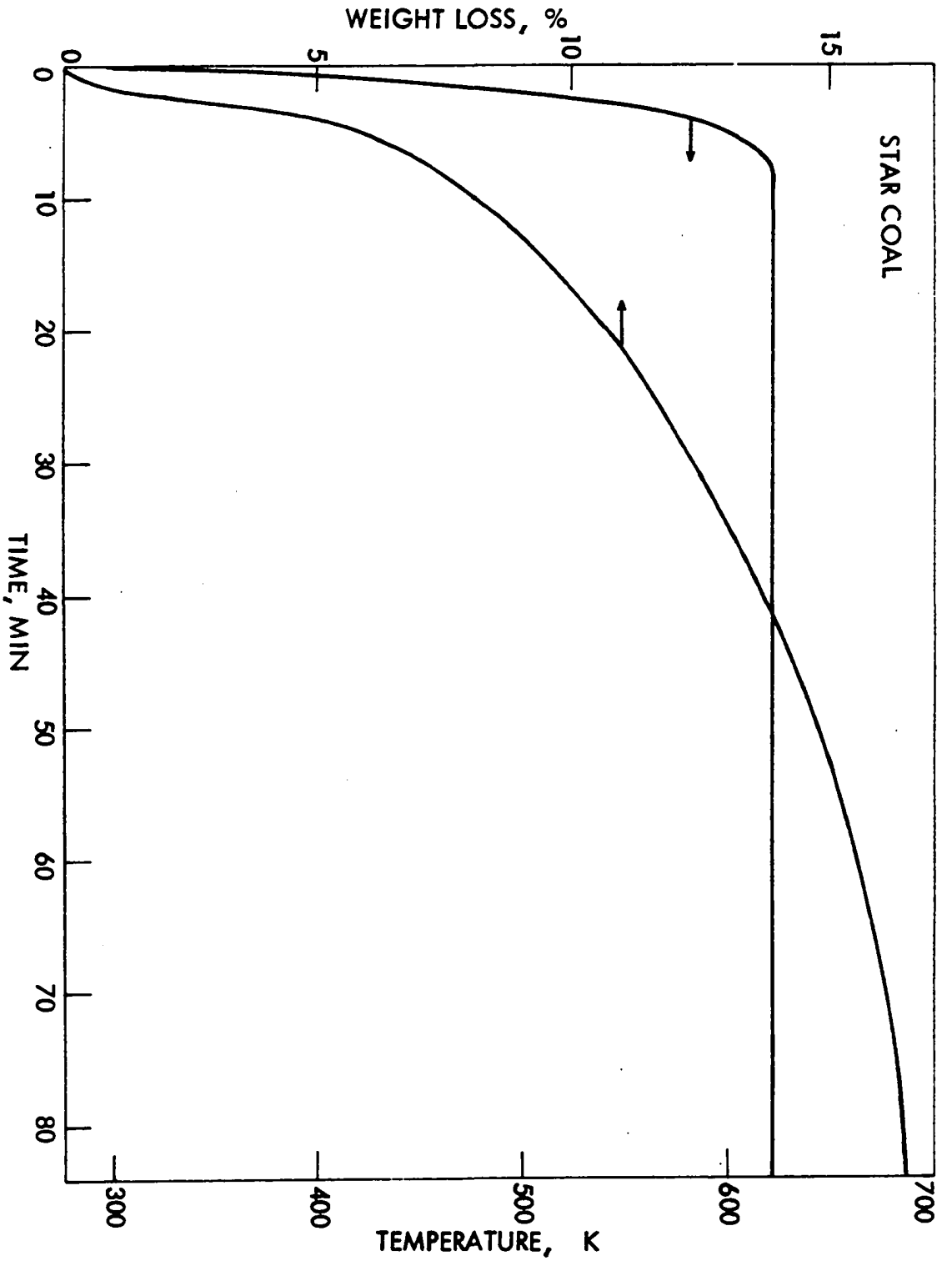
energy obtained in the primary decomposition region is about 10 Kcal/mole; in the secondary decomposition region it is about 1.5 Kcal/mole.

Devolatilization at constant temperature

When coal is heated to any temperature and then held there, a large portion of the volatile matter is released before it reaches a constant temperature. After the constant temperature is obtained, there is a relatively rapid weight loss at first; this occurs in less than 10 minutes and is followed by a prolonged period, about 40 minutes, where there is a steady, slower weight loss. Finally the rate of weight loss is very small and almost constant for a period of time. A typical weight-time diagram for Star coal at 744 K is shown in Figure 6. The temperature during the run also is shown on the figure.

The rate of reaction depends on the amount of volatile matter remaining in the coal sample. From the amount of volatile matter that has been released up to time t, V, and the ultimate amount of volatile matter that can be released at that temperature, V_0, the amount of volatile matter remaining in the coal sample, V_0-V, can be calculated. A semi-logarithm plot of the amount of volatile matter remaining in the coal versus time shows clearly the three stages of the devolatilization reaction once a

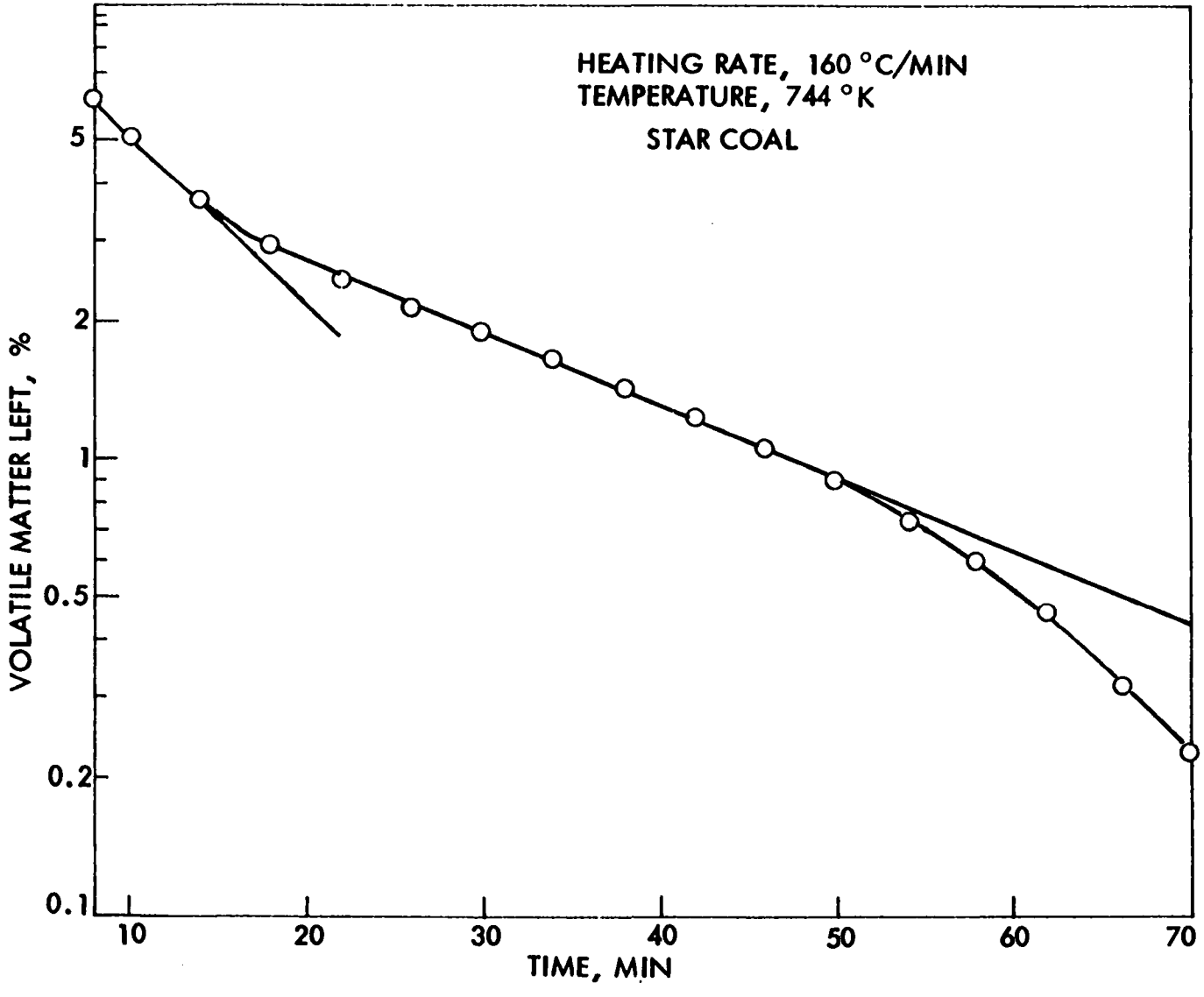
Figure 6. Typical weight loss curve of Star coal upon heating


WEIGHT LOSS, %
0
5
10
15
STAR COAL
TIME, MIN
0
10
20
30
40
50
60
70
80
TEMPERATURE, K
300
400
500
600
700

constant temperature is reached (Figure 7). The linear portion of this plot represents a first order reaction and its slope is the effective first order reaction rate constant. There is almost a two-fold difference between the slopes during the first stage of reaction and the second stage of reaction.

Three stages of reaction during constant temperature devolatilization were also reported by Shapatina et al. (1950) and Wiser et al. (1967). It appears that coal undergoes a thermal rupture of bonds within its structure when heated to temperatures between 300 °C and 500 °C. The products of thermal decomposition are dispersed throughout the coal mass and increase its fluidity. These fragments or free radicals will be released as volatile matter if they have a sufficiently high vapor pressure. However, most of them, being reactive, will seek stabilization by reacting with reactive species near them. The stabilization process, which may consist of cracking and condensing of the free radicals, results in the formation of a more stable solid residue and the evolution of some volatile products. This stabilization process is manifested by the decrease of fluidity during the second stage of reaction as demonstrated by Fitzgerald (1956a,b). The solid residue may further crack and rearrange its structure to release more volatile matter during the stabilization process.

Figure 7. Amount of volatile matter remaining in coal as a function of time


HEATING RATE, 160 °C/MIN
TEMPERATURE, 744 °K
STAR COAL
VOLATILE MATTER LEFT, %
5
2
1
0.5
0.2
0.1
10
20
30
40
50
60
70
TIME, MIN

This process, which is the third stage of reaction, is usually slow and involves small weight changes.

The rapid reaction stage spans the period when the coal mass shows an appreciable increase of fluidity. This suggests that the primary decomposition is the dominating factor during this period. The desorption of absorbed gases and moisture and thermal breakage of short-chain linkages within the coal structure is believed to account for this rapid rate of weight loss. The second reaction stage of steady weight loss is accompanied by a decrease in fluidity. This suggests the breakage of large side chains, which may contain one aromatic ring with varying attached side chains, and the condensation of free radicals to form solid products. The third reaction stage occurs after the coal mass resolidifies and shows little weight loss. The cracking and rearranging of the structure of the solid residue are considered the main reactions during this period. The devolatilization products are small molecule gases, such as CO and H_2. This view was supported by the experimental results of Shapatina et al. (1950).

For a simple reaction, the temperature dependence of the reaction rate constant should follow the Arrhenius equation:

$$k = k_0 e^{-\frac{E}{RT}} .$$

The Arrnehius plots for both the initial rapid reaction stage and the steady reaction stage are shown in Figure 8. For the first stage of reaction the rate constants can be correlated as

$$k = 0.2\, e^{-\frac{560}{T}}.$$

For the second stage of reaction, the rate constants can be correlated as

$$k = 0.12\, e^{-\frac{560}{T}}.$$

The effective activation energy observed is about 1.2 Kcal/mole for both stages.

Values of the activation energy for the devolatilization of coal reported by previous investigators vary from 2 to over 50 Kcal/mole. This wide range of variation is due to differences in the type of coal employed, the temperature range studied, and in the value chosen as the ultimate extent of reaction (V_0). Also, some studies were based on the evolution of a specific gas. The rate constants obtained in this experiment as compared to the rate constants from previous investigators as reviewed by Anthony and Howard (1976) are shown in Figure 9. The small temperature dependence of rate constants observed in this experiment suggests that different functional groups are reacting. The species decomposing at higher temperatures

Figure 8. Arrhenius plots for the initial rapid reaction stage and the steady reaction stage

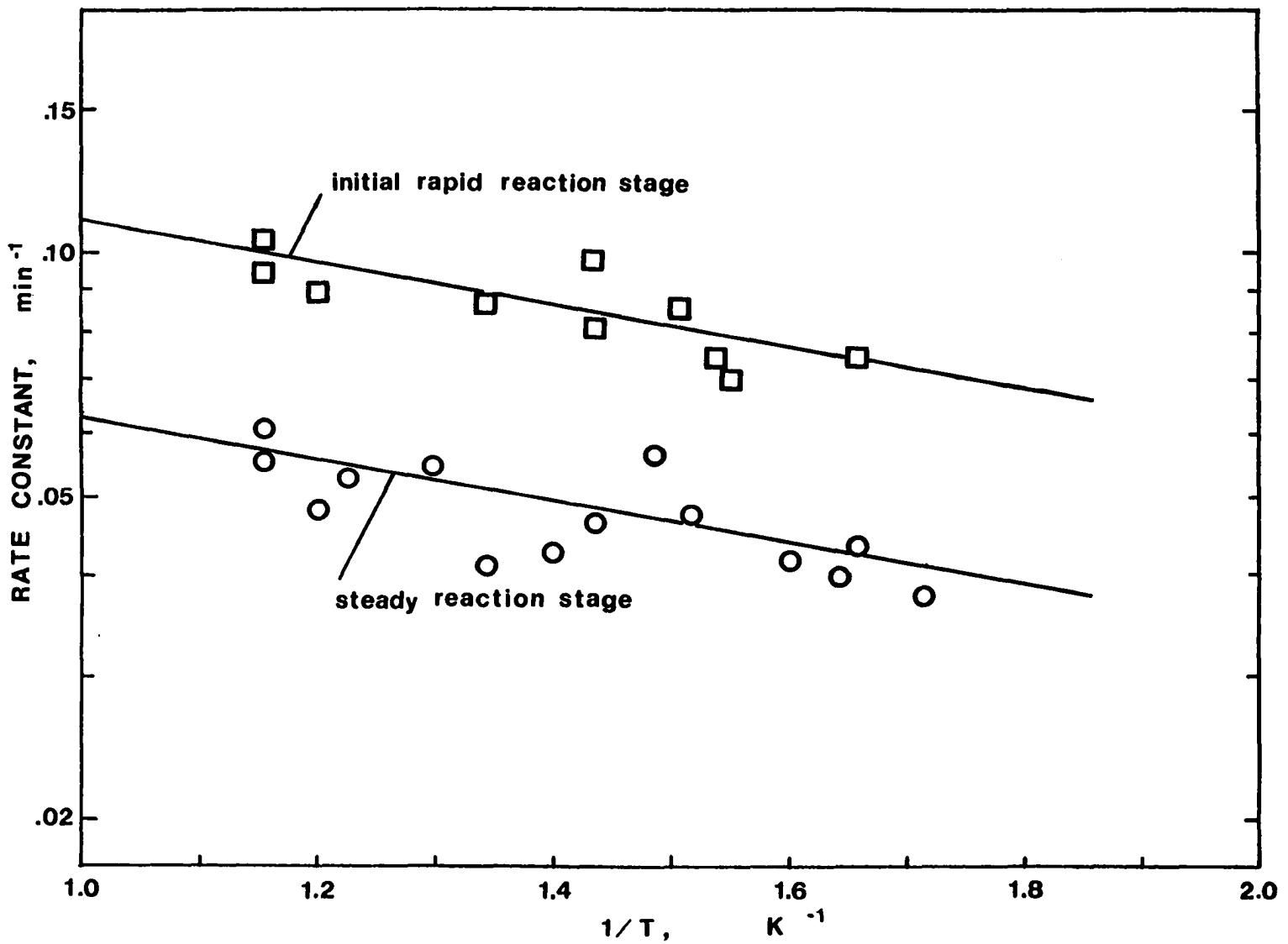
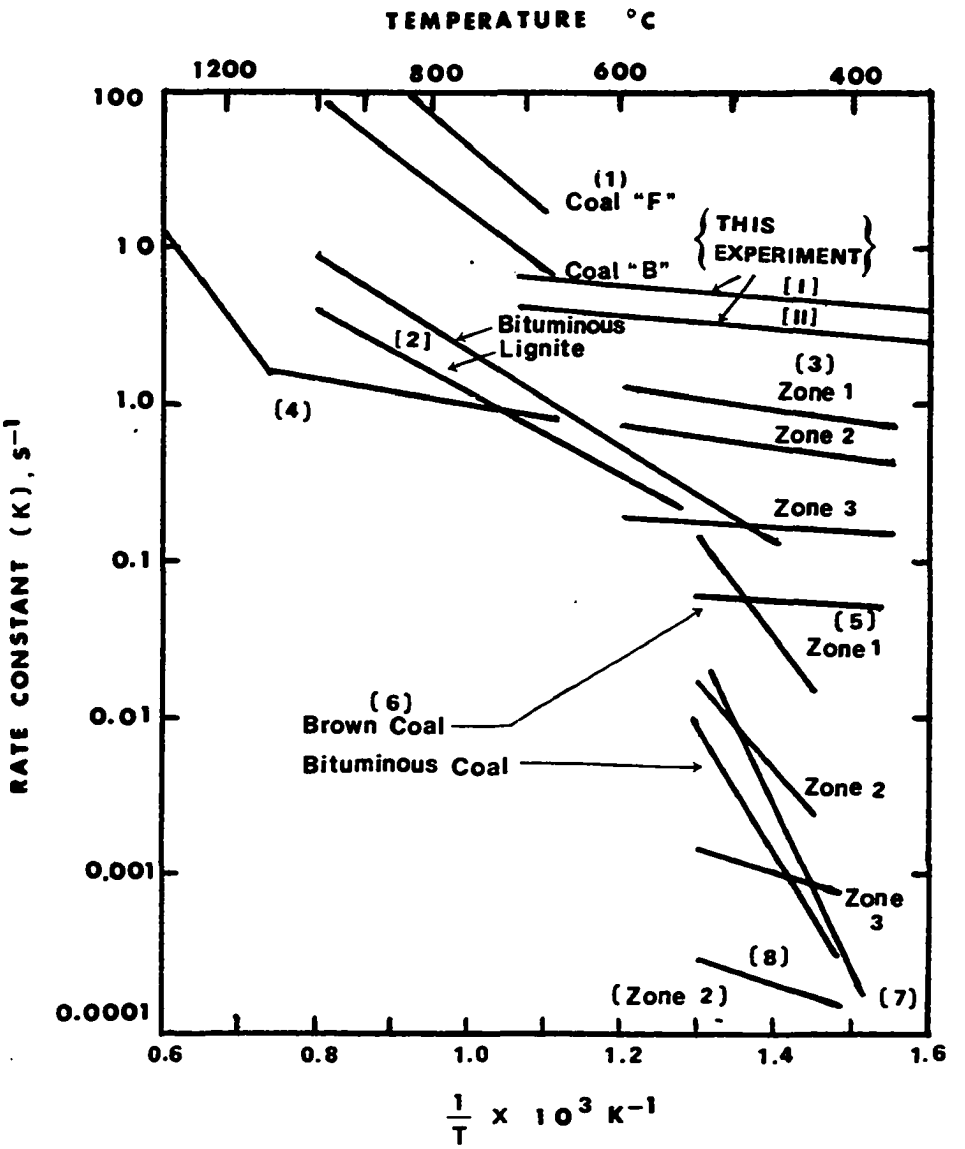

.15
.10
.05
.02
RATE CONSTANT, min -1
initial rapid reaction stage
steady reaction stage
1.0
1.2
1.4
1.6
1.8
2.0
1/T, K -1

Figure 9. Comparison of simple first-order coal devolatilization rate constants from different investigators (from Anthony and Howard, 1976)



Comparison of simple first-order coal devolatilization rate constants from different investigators [(1) Badzioch and Hawksley (1970), (2) Anthony et al. (1975), (3) Shapatina et al. (1960), (4) Howard and Essenhigh (1967), (5) Stone et al. (1954), (6) Van Krevelen et al. (1951), (7) Boyer (1952), (8) Wiser et al. (1967)].

may have larger activation energies and slower reaction rates, while the species decomposing at lower temperatures may have smaller activation energies and larger reaction rates. As a result, the temperature dependence observed for the rate of total weight loss is small.

Since devolatilization is the combined effect of numerous simultaneous reactions, a distribution of activation energies for the breakage of different bond linkages would be expected (Pitt, 1962; Anthony et al., 1976). A more general model for the devolatilization reaction would be as follows:

$$V_0(T) = \sum_i V_i^0(T)$$

$$V = \sum_i V_i$$

$$\frac{dV_i}{dt} = k_i(V_i^0 - V_i)$$

$$k_i = k_i^0 \exp(-\frac{E_i}{RT})$$

$$\frac{dV}{dt} = \sum_i k_i(V_i^0 - V_i)$$

$$= \sum_i k_i^0 \exp(-\frac{E_i}{RT})(V_i^0 - V_i)$$

The above equations are too complicated to use and the following simplified equations are used in the next section to describe the weight loss during constant-rate heating

period.

$$\frac{dV}{dt} \sim k(V_0-V)$$

$$\frac{dV}{dt} \sim k_0 \exp(-\frac{E}{RT})(V_0-V) \quad .$$

Devolatilization during constant rate heating

Because coal loses volatile matter during any preheating period, a nonisothermal, constant-rate heating process offers many advantages (Jüntgen and Van Heek, 1968). For instance, the reaction always starts under definite conditions, the reaction can be studied in one run over the entire temperature range of interest, and it simulates better commercial coal processing which usually takes place with increasing temperature.

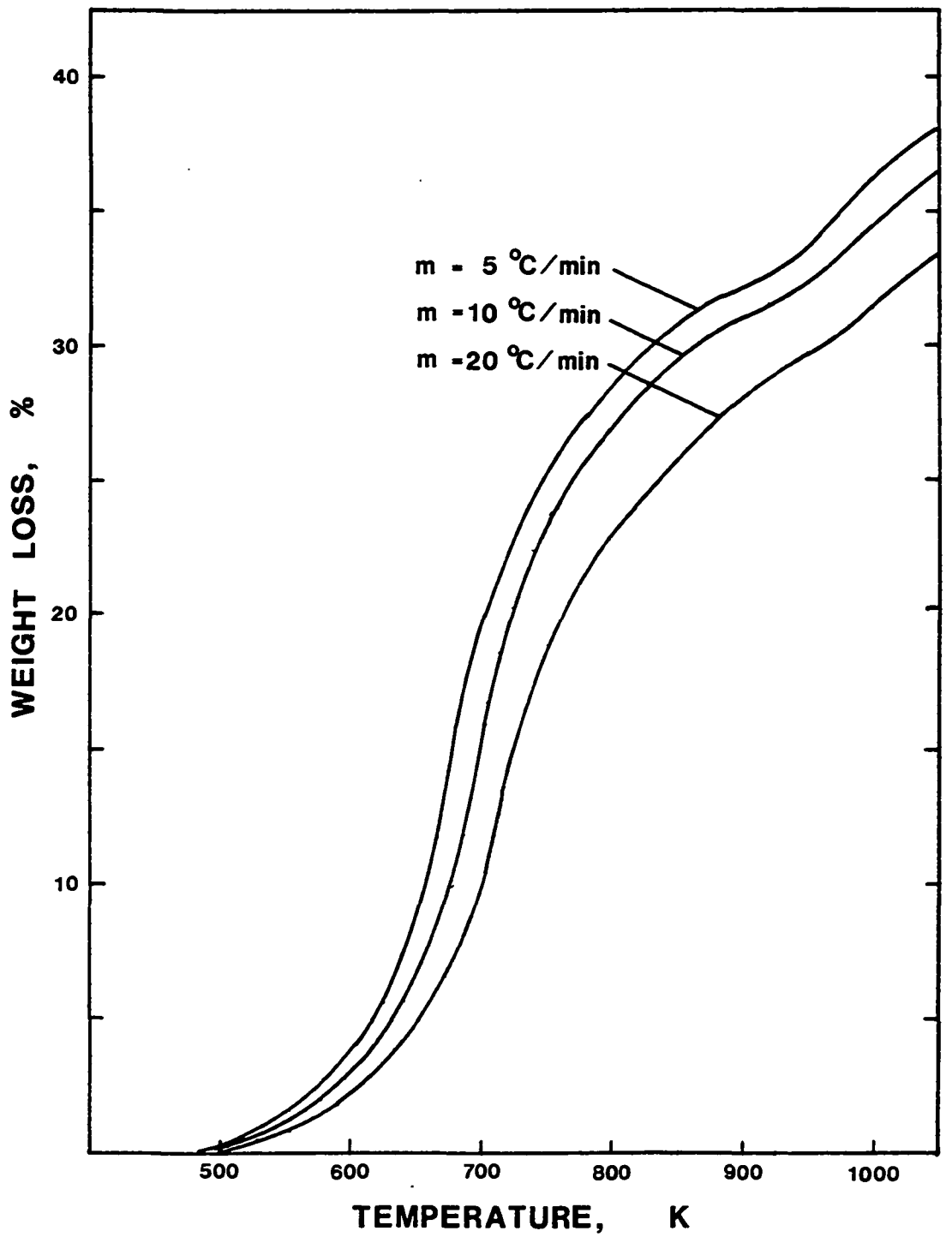
A plot of the sample weight loss as a function of temperature during a nonisothermal, constant-heating rate run produces an s-shaped curve. This curve shifts to a higher temperature level as the rate of heating increases (Figure 10).

For a constant-heating rate process with a heating rate of m °C/min,

$$\frac{dT}{dt} = m \quad .$$

Assuming that the devolatilization reaction follows first-

Figure 10. Weight loss curves for different heating rates


40
30
20
10
WEIGHT LOSS, %
m - 5 °C/min
m -10 °C/min
m -20 °C/min
500
600
700
800
900
1000
TEMPERATURE, K

order reaction kinetics,

$$\frac{dV}{dt} = k(T)\,[V_0(T)-V] \ ,$$

then

$$\frac{dV}{dT} = \frac{k(T)}{m}\,[V_0(T)-V] \ ,$$

or

$$\frac{dV}{dT} + \frac{k(T)}{m}\,V = \frac{k(T)}{m}\,V_0(T)$$

with the initial condition that at t=0,

$$T = T_0, \quad V = 0 \quad \text{and} \quad V_0(T_0) = 0$$

where T_0 is the starting temperature, namely room temperature (293 K). The solution of this differential equation is

$$V = e^{-\int \frac{k(T)}{m} dT} \left[\int_{T_0}^{T} e^{\int \frac{k(T)}{m} dT} \frac{k(T)}{m}\, V_0(T)\, dT\right]$$

Upon integration by parts,

$$V = V_0 - e^{-\int \frac{k(T)}{m} dT} \int_{T=T_0}^{T=T} e^{\int \frac{k(T)}{m} dT}\, dV_0$$

Dividing through by V_0 and rearranging yields

$$\frac{V}{V_0} = 1 - \frac{\int_{T=T_0}^{T=T} e^{\int \frac{k(T)}{m} dT} \, dV_0}{e^{\int \frac{k(T)}{m} dT} V_0}$$

This solution satisfies many of the conditions observed in the experiment. (The proof of these are given in Appendix A).

i) The weight loss at a given temperature is between the ultimate weight loss and zero, $0 < \frac{V}{V_0} < 1$.

ii) At a given temperature, the weight loss decreases as the heating rate increases, $(\frac{\partial V}{\partial m})_T < 0$.

iii) The weight loss approaches zero as the heating rate approaches infinite, $\lim_{m \to \infty} V = 0$.

iv) The weight loss approaches the ultimate weight loss as the heating rate approaches zero, $\lim_{m \to 0} V = V_0$.

Knowing the functional relationships between $V_0(T)$, $k(T)$ and the temperature, the weight loss curves for different heating rates can be predicted. The relationship between $V_0(T)$ and temperature has already been shown in

Figure 4. The weight loss during the constant-rate heating process is dominated by the primary decomposition. Therefore, the correlation of the rate constants for the first stage of the reaction were used, i.e., $k = 0.2\, e^{-\frac{560}{T}}$.

For a given $V_0(T)$ there is a corresponding temperature, so the integral, $\int^T \frac{k(T)}{m}\, dT$, can be calculated.

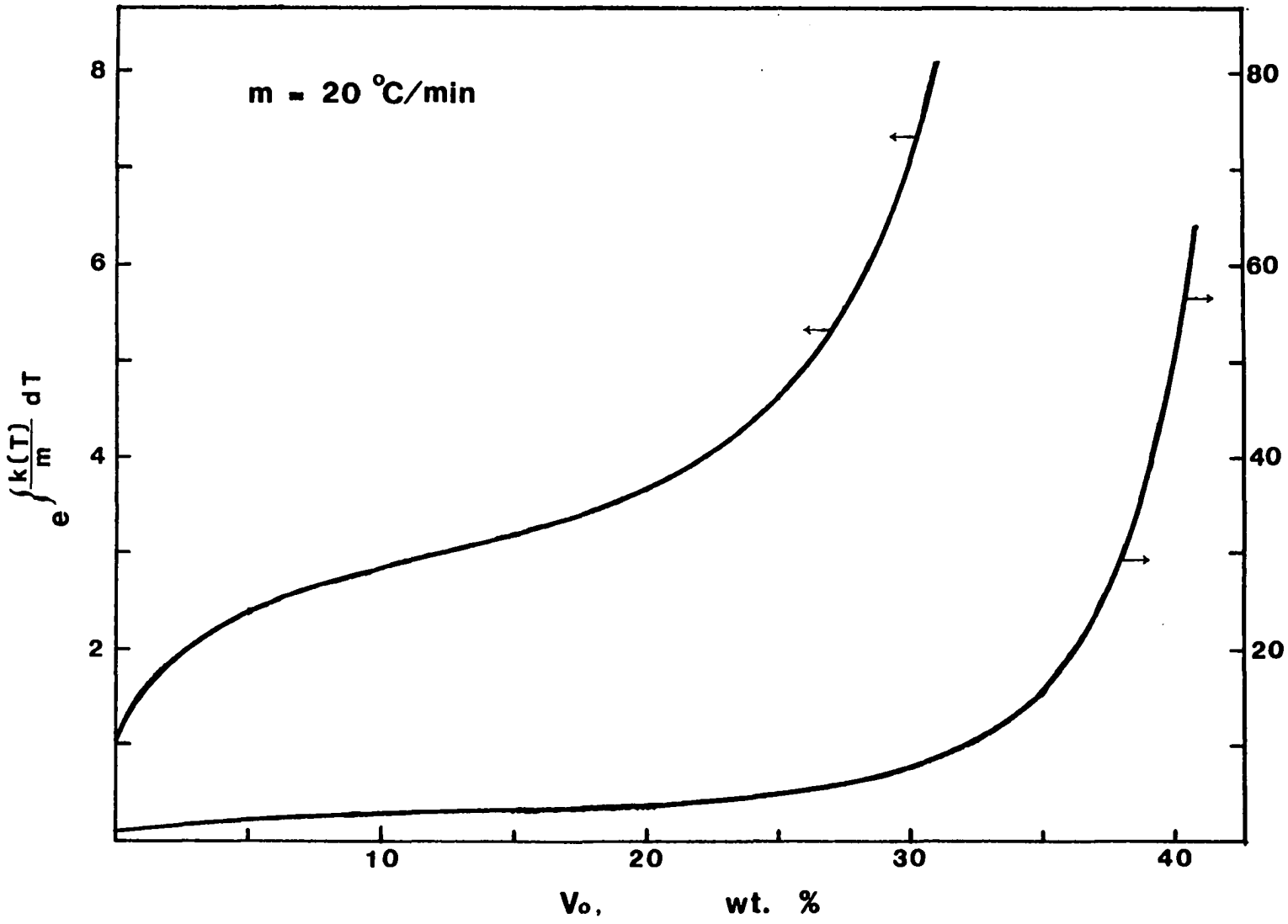
$$\int_0^T \frac{k(T)}{m}\, dT = \frac{k_0}{m} \int_0^T e^{-\frac{560}{T}}\, dT$$

$$= \frac{560\ k_0}{m} \int_0^x e^{-\frac{1}{x}}\, dx \qquad (x = \frac{T}{560})$$

$$\int_0^x e^{-\frac{1}{x}}\, dx = xe^{-\frac{1}{x}} - \int_{\frac{1}{x}}^{\infty} \frac{e^{-y}}{y}\, dy$$

The integral $\int_{\frac{1}{x}}^{\infty} \frac{e^{-y}}{y}\, dy$ is the exponential integral $E_1(\frac{1}{x})$, which is tabulated in many mathematical tables (Abramowitz and Stegun, 1965). The values of $e^{\int_0^T \frac{k(T)}{m}\, dT}$ for m = 20 °C/min were calculated and plotted as a function of V_0 as shown in Figure 11. By using numerical integration from the plot of $e^{\int_0^T \frac{k(T)}{m}\, dT}$ versus V_0, $\frac{V}{V_0}$ can be calculated. The calculation procedures for other heating

Figure 11. Graphical method for calculating weight loss curve


m = 20 °C/min
8
6
4
2
80
60
40
20
10
20
30
40
$e^{\int \frac{k(T)}{m} dT}$
Vo, wt. %

rates are the same. The experimental and calculated weight loss curves for heating rates of 5, 10 and 20 °C/min. are shown in Figures 12, 13 and 14.

It is also possible to calculate the temperature at which the maximum rate of weight loss occurs (peak temperature) from the following equations:

$$V' = \frac{k(T)}{m}[V_0 - V]$$

$$V'' = \frac{k(T)}{m}\left[\frac{E}{RT^2}(V_0 - V) + (V_0' - V')\right]$$

at the peak temperature

$$V'' = 0$$

Thus

$$V_0'(T) = \left(\frac{k(T)}{m} - \frac{E}{RT^2}\right) \frac{\int_{T=T_0}^{T=T} e^{\int \frac{k(T)}{m}\,dT}\, dV_0}{e^{\int \frac{k(T)}{m}\,dT}}$$

Therefore, if $V_0'(T)$ and $\left(\frac{k(T)}{m} - \frac{E}{RT^2}\right)\frac{\int_{T_0}^{T} e^{\int \frac{k(T)}{m}\,dT}\, dV_0}{e^{\int \frac{k(T)}{m}\,dT}}$ are plotted versus temperature on the same figure, the temperature at which these two curves intersect each other is the predicted peak temperature. Figure 15 is such a plot for heating rates of 5, 10 and 20 °C/min. The peak temperatures predicted and observed in the experiments are listed below:

Figure 12. Comparison of experimental and calculated weight loss curves for Star coal (heating rate 5 °C/min)

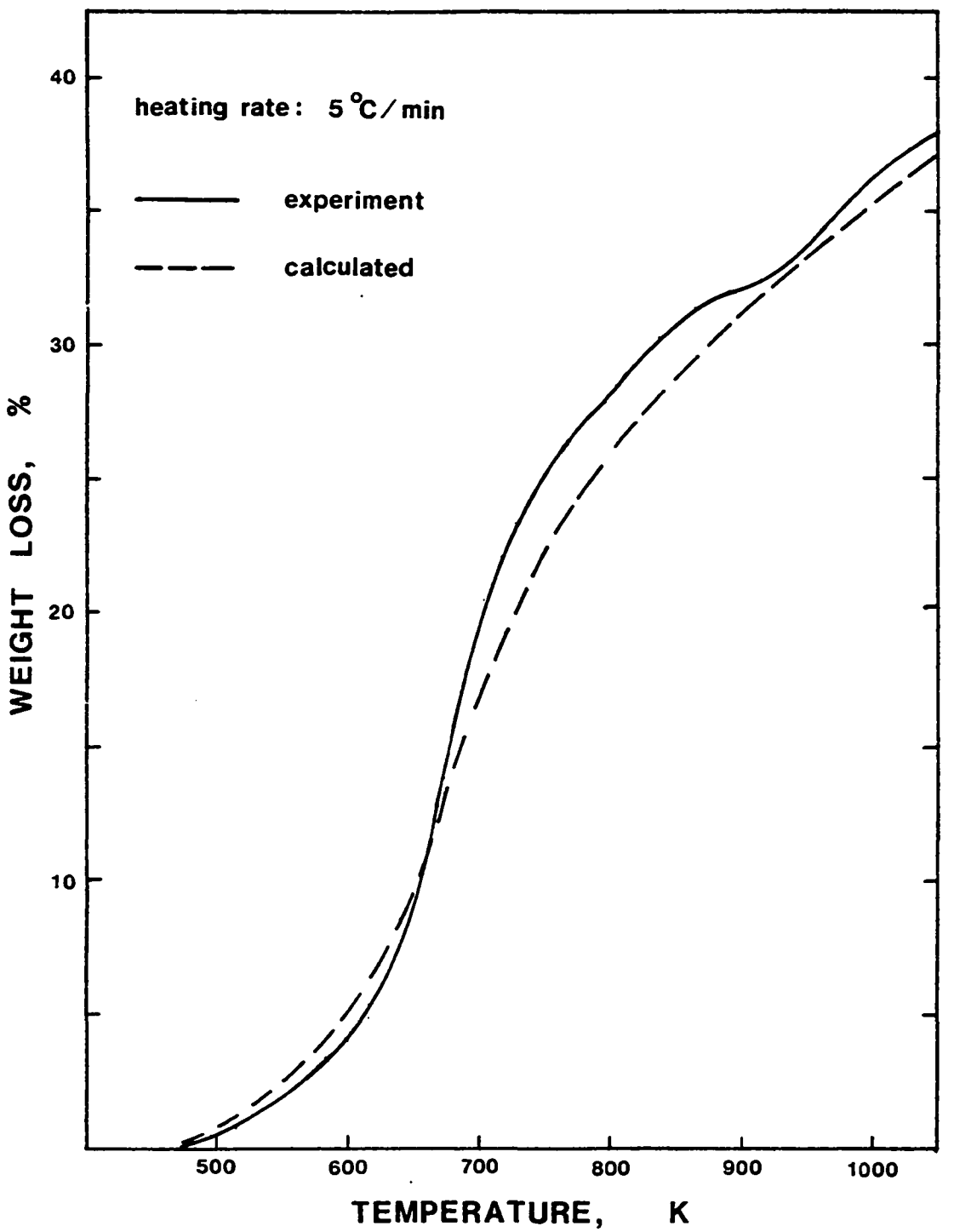

heating rate: 5 °C / min
experiment
calculated
WEIGHT LOSS, %
40
30
20
10
500
600
700
800
900
1000
TEMPERATURE, K

Figure 13. Comparison of experimental and calculated weight loss curves for Star coal (heating rate 10 °C/min)

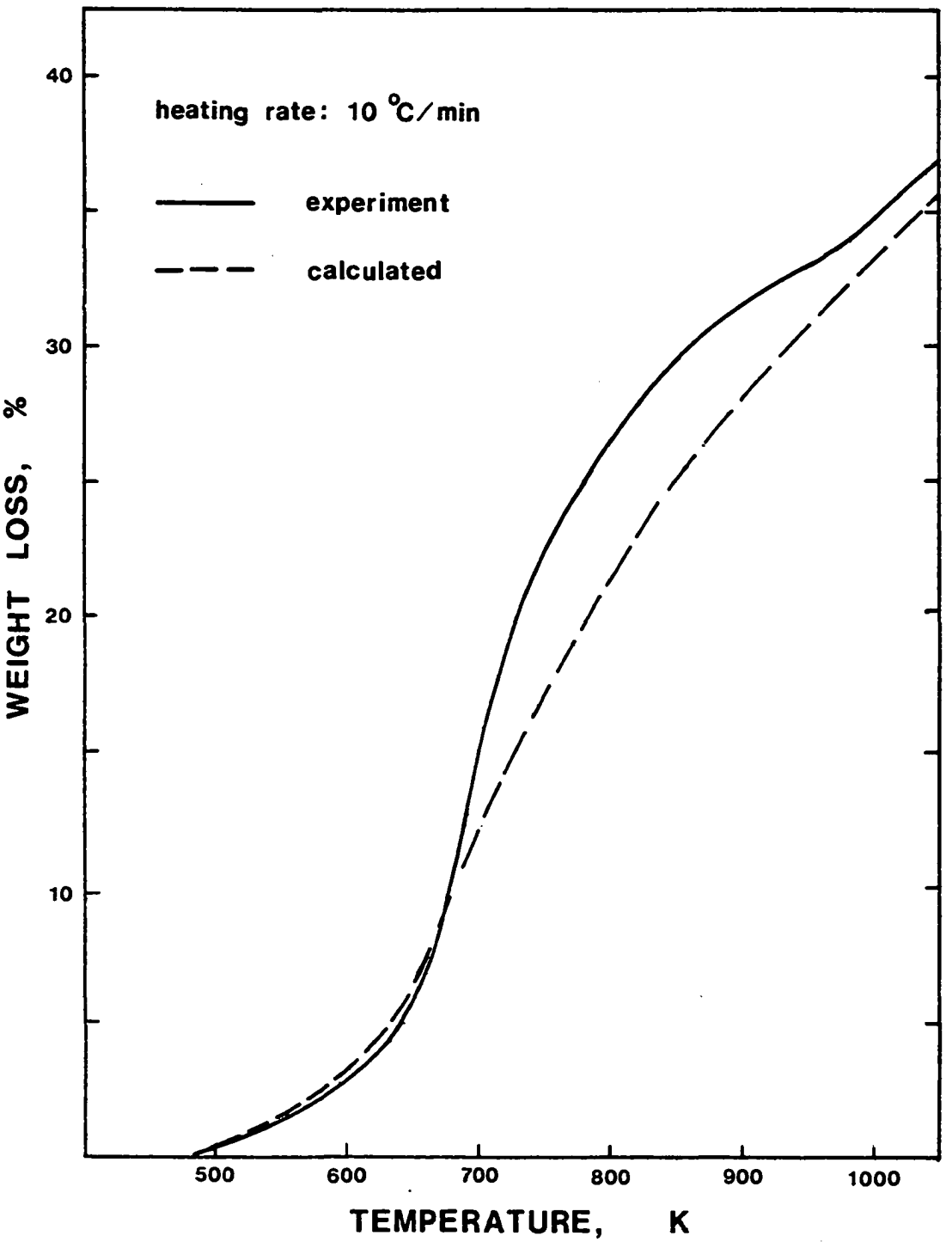

heating rate: 10 °C/min
experiment
calculated
WEIGHT LOSS, %
40
30
20
10
500
600
700
800
900
1000
TEMPERATURE, K

Figure 14. Comparison of experimental and calculated weight loss curves for Star coal (heating rate 20 °C/min)

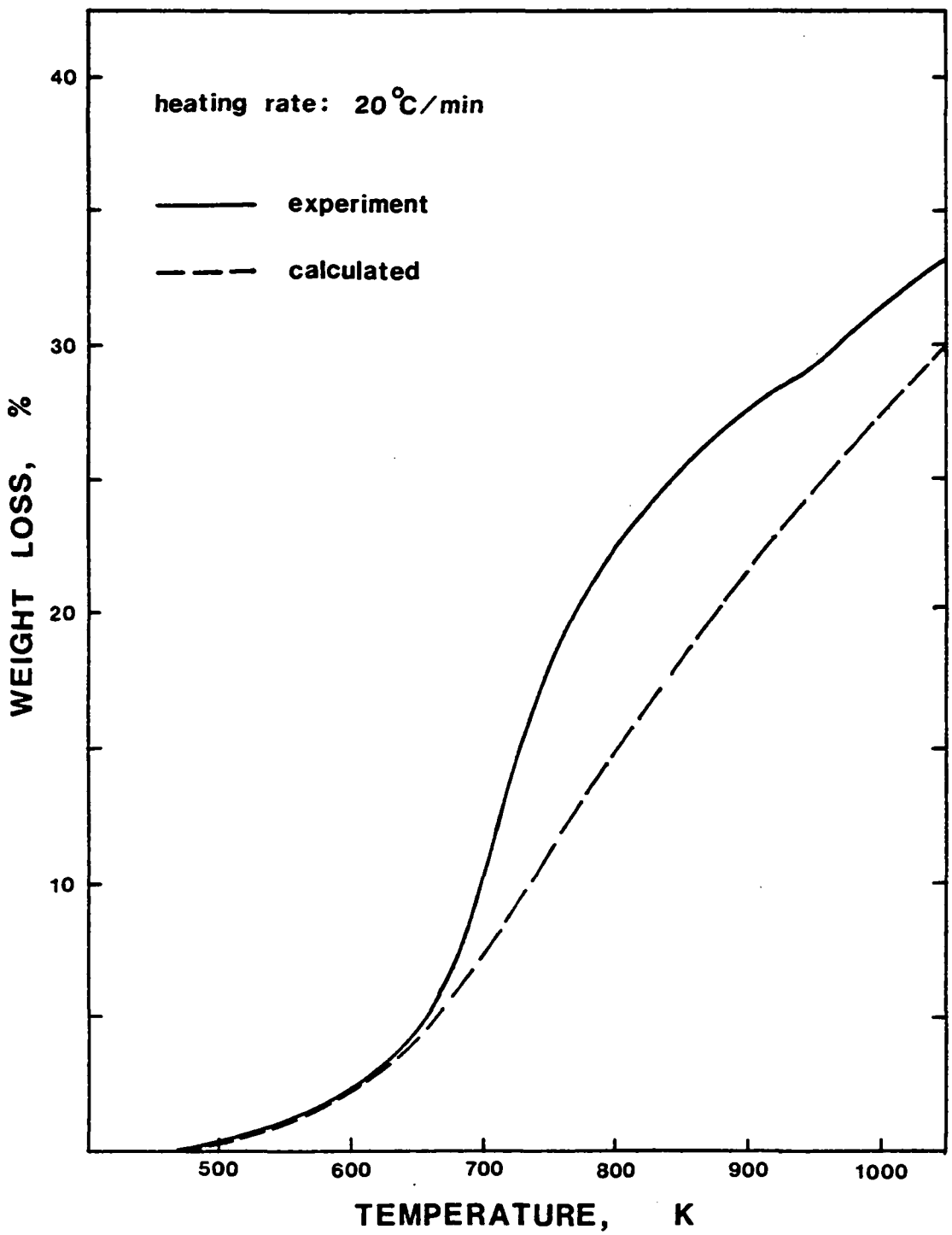
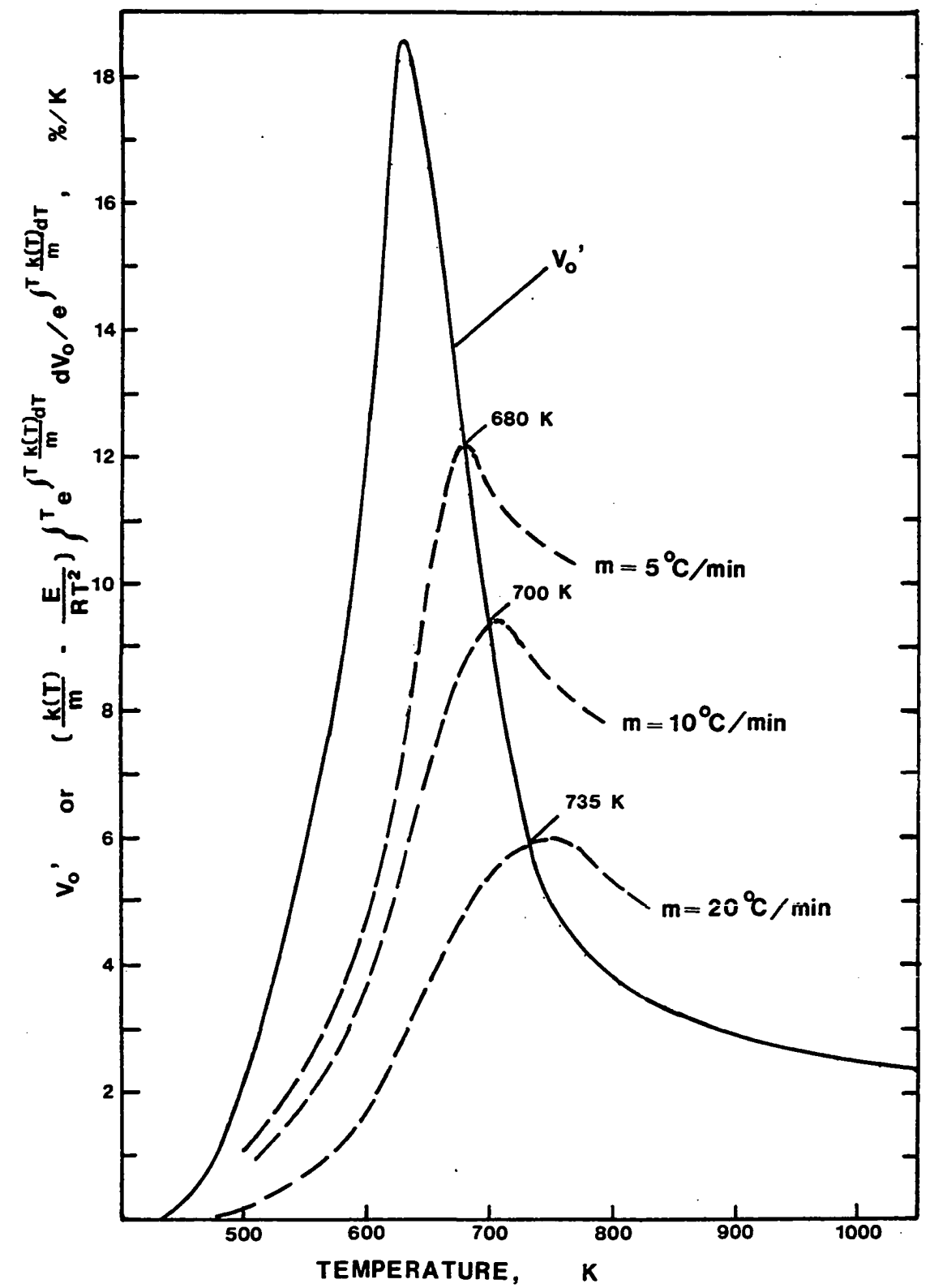

heating rate: 20 °C/min
experiment
calculated
WEIGHT LOSS, %
40
30
20
10
500
600
700
800
900
1000
TEMPERATURE, K

Figure 15. Graphical method for predicting peak temperatures


V_o' or $(\frac{k(T)}{m} - \frac{E}{RT^2}) \int^T e^{\int^T \frac{k(T)}{m} dT} dV_o / e^{\int^T \frac{k(T)}{m} dT}$, %/K
18
16
14
12
10
8
6
4
2
500
600
700
800
900
1000
TEMPERATURE, K
V_o'
680 K
m = 5 °C/min
700 K
m = 10 °C/min
735 K
m = 20 °C/min

	Heating Rate	5 °C/min	10 °C/min	20 °C/min
Peak Temperature, K	experimental	673	703	723
	predicted	680	700	735

In general, the proposed model agrees with the experimental results. It explains the dependence of weight loss on temperature and heating rate and also closely predicts the peak temperatures for different heating rates. There are, however, some deviations between the theoretical values and the weight loss observed in the experiments. These differences are larger in the high temperature region and become more pronounced as the heating rate increases. This deviation is probably due to differences in the reaction products. Between 550 and 750 K, the products are from the primary decomposition and include CO_2, CO, high hydrocarbon gases and tar, while above 750 K the main constituents of volatile matter come from the secondary decomposition and are gases such as H_2, CH_4 and CO. Also, weight is used as the concentration basis in the proposed model instead of moles. The products of primary decomposition have larger molecular weights than the products of the secondary decomposition. It appears that the proposed reaction

model is more satisfactory in the primary decomposition region than in the secondary decomposition.

The primary decomposition occurs rather rapidly throughout the whole coal mass. Those decomposition products with sufficient vapor pressure have to diffuse through the coal pores to the surface before they can be released as volatile matter. Because of the limitation of diffusion, there may be a pressure build-up within the pore space of the coal mass during the initial rapid reaction period. This pressure build-up has been discussed extensively by Berkowitz (1960). The extent of pressure build-up depends on the rate of heating. The faster the heating rate, the less the amount of volatile matter released during the heating period and the greater will be the pressure build-up. This will result in a shifting of the effect of the reaction to higher temperatures for the fast heating process. Also, during the initial degasification period, some of the free radicals from the primary decomposition may be carried away by the gases evolved and incorporated in the tar before going through further decomposition. The "transport effect" as suggested by Van Krevelen et al. (1956) and Yellow (1965) is more pronounced as the heating rate increases. This is another factor that contributes to higher weight losses for the high heating-rate processes.

Summary and Comments

The devolatilization of Iowa coal was studied by a thermogravimetric method at temperatures under 750 °C. The ultimate volatile matter released was found to be only a function of temperature under the experimental conditions. The devolatilization at a constant temperature condition was found to have three reaction stages and the reaction was largely first order. A model was derived to predict the weight losses during the constant heating-rate process for different heating rates. The model explains the experimental results well.

The laboratory results are usually obtained under controlled and idealized conditions. The reaction mechanism may become more complicated in real industrial processes. Davis and Brown (1967) studied the thermal decomposition of spherical bituminous particles with diameters in the range of 0.625-2.5 cm. They indicated that the initial rate of weight loss was determined by the convective heat flux to the particle. Mazumdar and Chatterjee (1973) have noted that the postulates of the mechanism of primary pyrolysis are strictly followed only under ideal conditions, e.g., in thin beds with rapid rates of heating as in fluidized beds and transport reactors. Due to the interaction between the potential tar-forming constituents and the incipient

coke-forming substance, the yields of solid product and tar are partially interconvertible. The greater the thickness of the coal bed, the greater is the solid yield. These investigators have shown that particle size, geometrical arrangement of the reactor and the flow rate of carrier gas all have some influence on devolatilization in real practice. In the presence of these physical limitations, the reaction model from the laboratory results may need to be modified.

DESULFURIZATION

Introduction

The sulfur in coal appears in organic and inorganic forms. The inorganic sulfur includes pyrite (FeS_2) and sulfate ($FeSO_4$, $CaSO_4$ etc.). The content of sulfate in coal is usually small and does not present too much of a problem. Some of the pyrites in coal is in the form of distinctive layers or large nodules which can be separated easily by crushing and treatment in conventional washing processes. However, a portion of the pyrite is present as small crystals embedded in the carbonaceous material and these are distributed all through the coal. These pyrite crystals, along with the organic sulfur, can not be removed by ordinary coal cleaning processes (Leonard and Cockrell, 1970; Leonard et al., 1967).

There is no direct evidence of how the organic sulfur is present in coal. However, from solvent extraction and pyrolysis studies, infrared (i.r.) and nuclear magnetic resonance (n.m.r.) spectra and various other experiments, it is believed that sulfur compounds in coal occur as mercaptans (PhSH), sulfides (PhSPh'), disulfides (PhS-SPh') or thiophenes [ ,  etc.) (Given and Wyss, 1971; Dryden, 1963; Thiessen, 1935).

Since this study dealt with coal desulfurization during gas treatment at elevated temperatures, a review of the reactions of the various sulfur forms under these conditions is of interest.

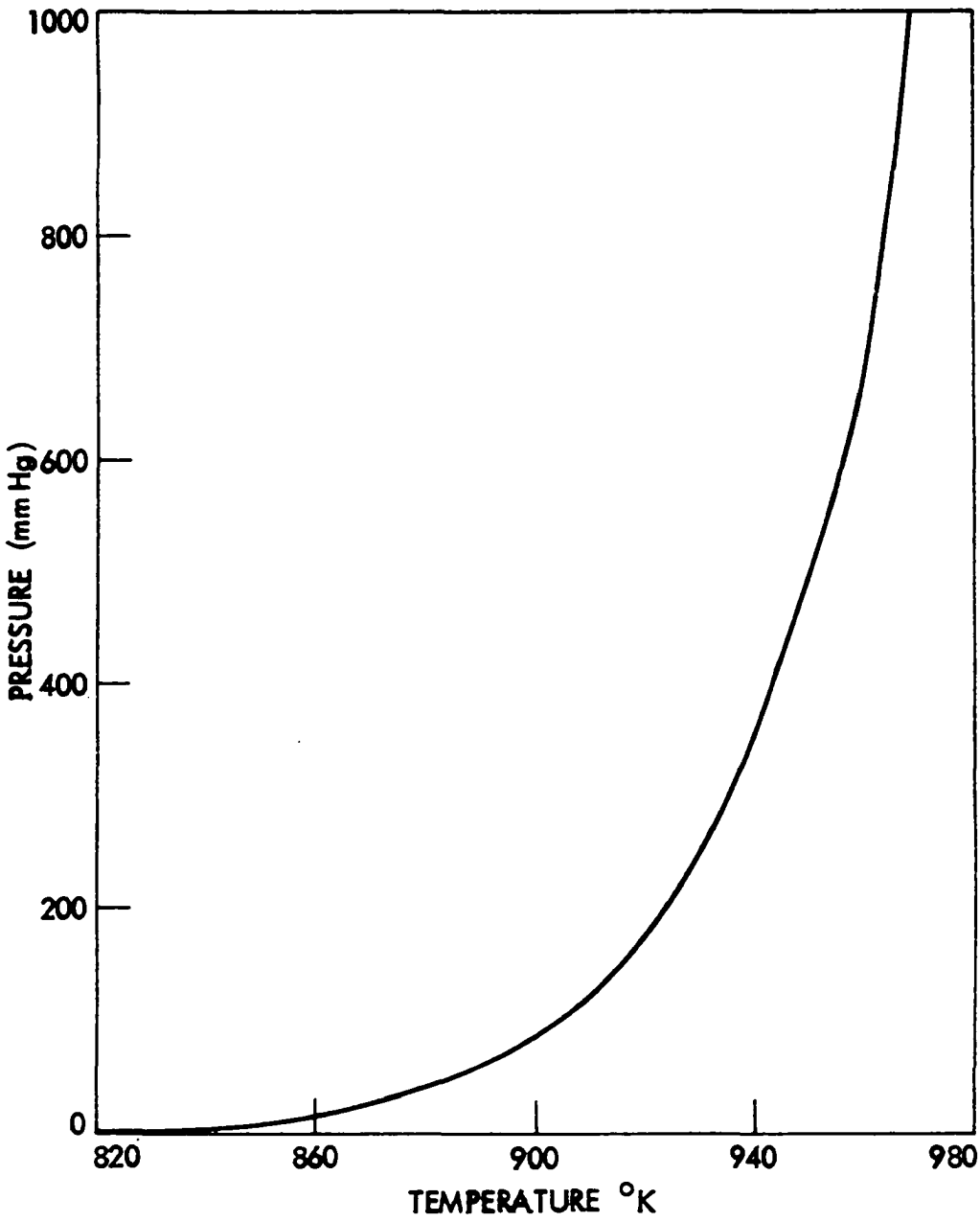
Pyrite has two different crystalline forms, cubic pyrite and rhombic marcasite. In general, they have similar chemical properties. Upon heating in an inert atmosphere, pyrite decomposes to ferrous sulfide (FeS) and volatile sulfur:

$$FeS_2 \rightarrow FeS + \frac{1}{2} S_2.$$

The reaction starts at 500 °C and becomes rapid at 700 °C. The decomposition product, ferrous sulfide, is rather stable up to 1300 °C. The equilibrium vapor pressure of sulfur over pyrite at 1 atm total pressure is shown in Figure 16.

The chemical reactions of pyrite in an oxidizing atmosphere are extremely complicated. Ferrous sulfide (FeS), ferrous oxide (FeO), ferric oxide (Fe_2O_3), magnetite (Fe_3O_4), ferrous sulfate ($FeSO_4$), and ferric sulfate ($Fe_2(SO_4)_3$) are all reported to be found in the reaction products. The gaseous products include sulfur dioxide (SO_2), sulfur trioxide (SO_3) and elemental sulfur. At atmospheric pressure, the reactions start at about 350 °C and include:

Figure 16. Vapor pressure of sulfur over pyrite at 1 atm.


1000
800
600
400
200
0
PRESSURE (mm Hg)
820
860
900
940
980
TEMPERATURE °K

$$FeS_2 + O_2 \rightarrow FeS + SO_2$$

$$FeS + \frac{3}{2} O_2 \rightarrow FeO + SO_2$$

$$2FeS + \frac{7}{2} O_2 \rightarrow Fe_2O_3 + 2SO_2$$

The equilibrium constants of various reactions of pyrite in oxidizing gases are shown as a function of temperature in Figure 17.

In a hydrogen atmosphere, the reactions of pyrite are slower. The following reactions have been reported:

$$FeS_2 + H_2 \rightarrow FeS + H_2S$$

$$FeS + H_2 \rightarrow Fe + H_2S$$

The rate of the first reaction becomes appreciable at about 280 °C, while the rate of the second reaction is not appreciable until 370 °C.

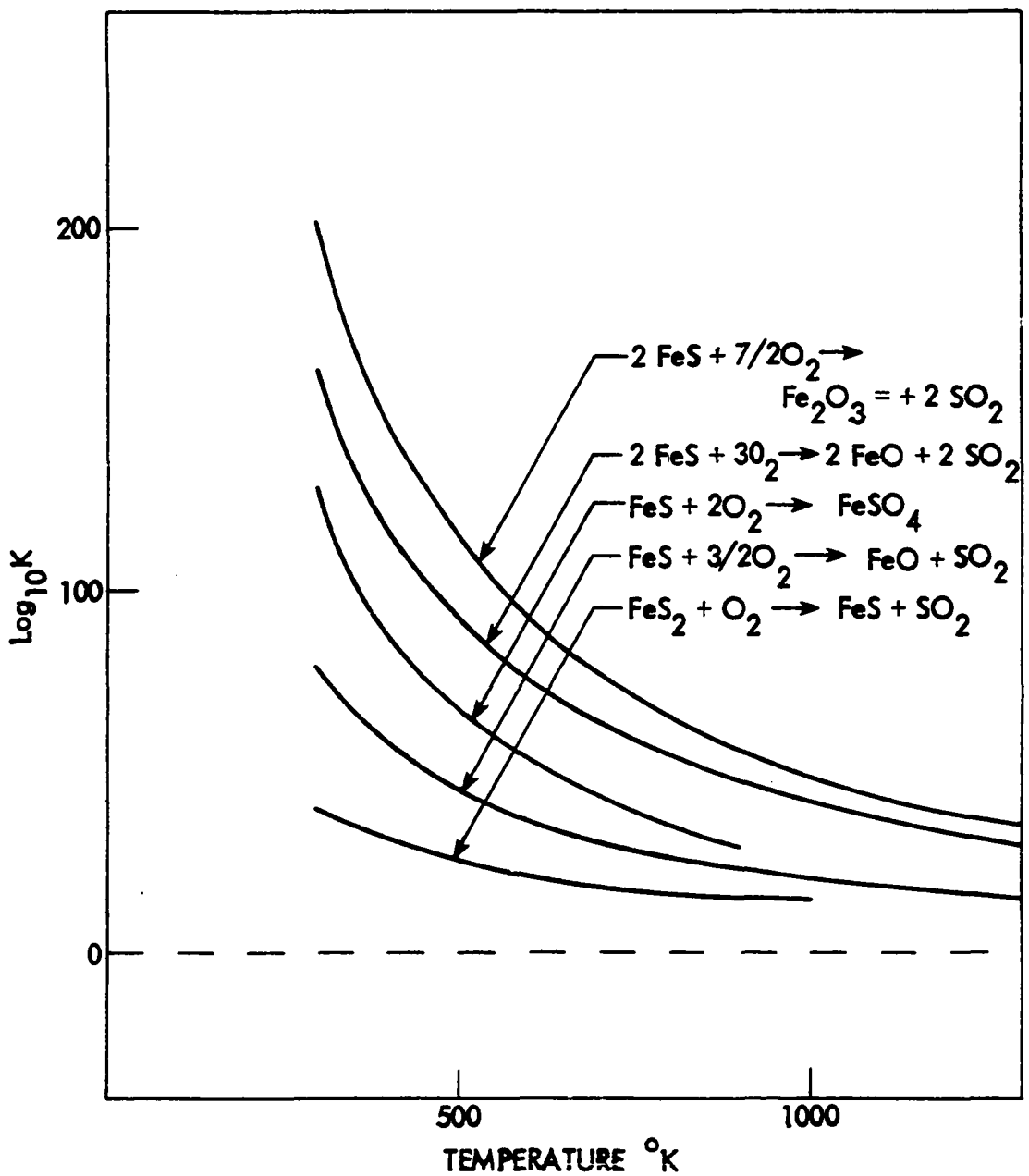
Pyrite also is attacked by steam. In a superheated steam atmosphere at temperatures of 400-600 °C, a greater extent of decomposition of the pyrite is achieved than in a nitrogen atmosphere.

The possible chemical reactions are:

$$3FeS_2 + 2H_2O \rightarrow 3FeS + 2H_2S + SO_2$$

$$FeS + H_2O \rightarrow FeO + H_2S$$

Figure 17. Equilibrium constants for reactions of pyrite in oxidizing gas

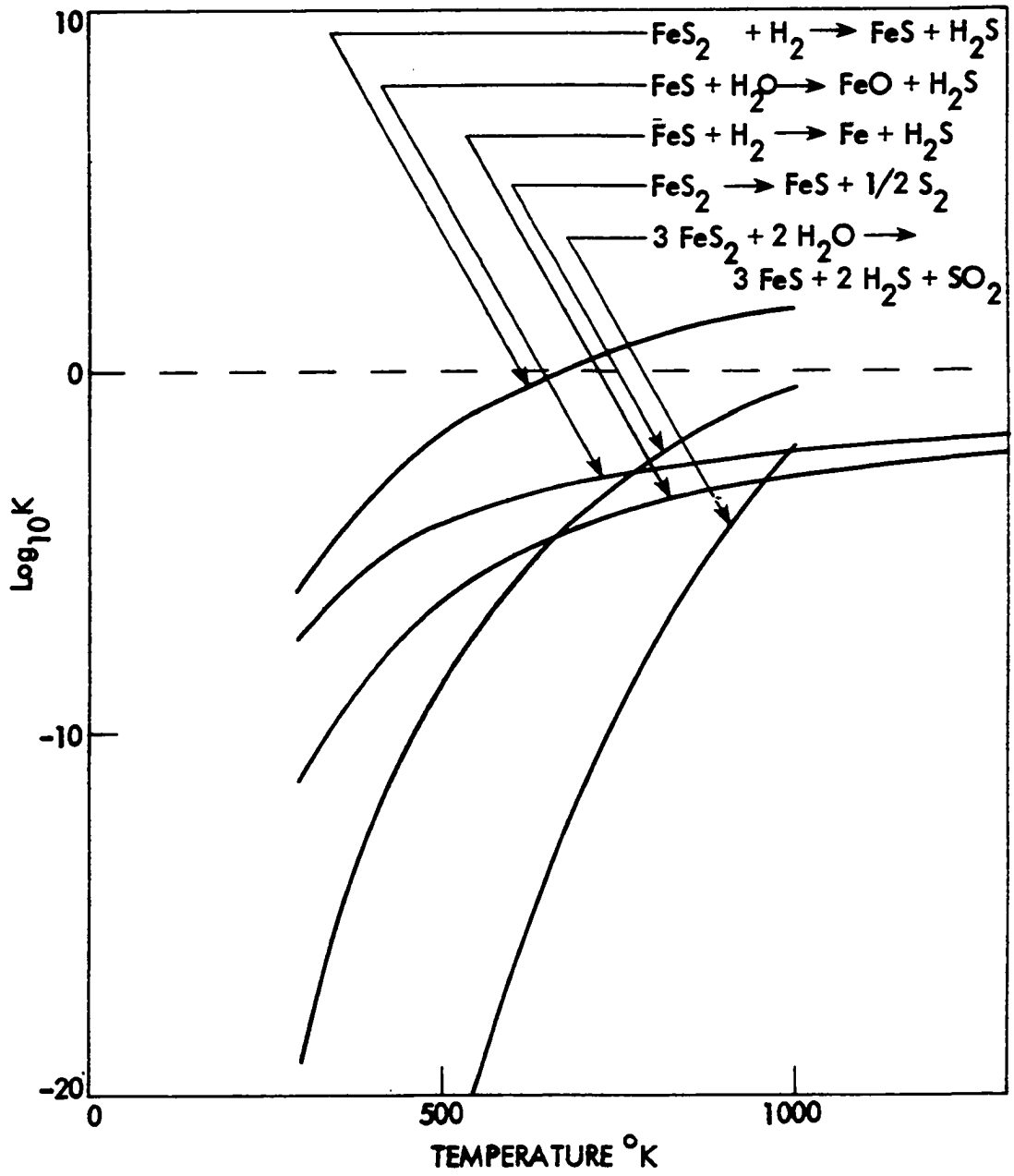

200
100
0
$Log_{10}K$
$2\,FeS + 7/2O_2 \rightarrow Fe_2O_3 = + 2\,SO_2$
$2\,FeS + 3O_2 \rightarrow 2\,FeO + 2\,SO_2$
$FeS + 2O_2 \rightarrow FeSO_4$
$FeS + 3/2O_2 \rightarrow FeO + SO_2$
$FeS_2 + O_2 \rightarrow FeS + SO_2$
500
1000
TEMPERATURE °K

The equilibrium constants for the reactions of pyrite in hydrogen and steam as a function of temperature are shown in Figure 18 (Meller, 1935; Knacke, 1973).

Because of a lack of knowledge concerning the molecular structure of coal, the chemical reactions of the organic sulfur compounds in coal remain highly speculative. In an inert atmosphere, mercaptans yield hydrogen sulfide, sulfur hydrocarbons, sulfides and a tarry residue when heated to temperatures below 500 °C. Sulfides start to decompose at about 400 °C and release gaseous hydrocarbons, hydrogen sulfide and some mercaptans. Disulfides yield a similar range of products as sulfides plus sulfur. Thiophenes are usually stable at low temperature. During pyrolysis of coal, most of the organic sulfur released is in the form of hydrogen sulfide, with a small fraction of mercaptans and alkyl sulfides (Thiessen, 1945).

In a hydrogen atmosphere, mercaptans, sulfides, disulfide and thiophenes can be reduced to hydrogen sulfide and the parent hydrocarbons. These reactions are all thermodynamically favorable at temperatures under 750 °C. However, they are kinetically restricted and have to be carried out under high hydrogen partial pressure and with suitable catalysts such as Raney nickle or cobalt molybdate. The desulfurization reactions under low hydrogen pressure are believed mostly to be the breakage of sulfur containing com-

Figure 18. Equilibrium constants for reactions of pyrite with hydrogen and steam


10
0
-10
-20
0
500
1000
TEMPERATURE °K
Log10K
FeS2 + H2 → FeS + H2S
FeS + H2O → FeO + H2S
FeS + H2 → Fe + H2S
FeS2 → FeS + 1/2 S2
3 FeS2 + 2 H2O →
3 FeS + 2 H2S + SO2

pounds from the coal matrix. The extent of secondary hydrogenation of the decomposed sulfur compounds possibly are small.

In an oxidizing atmosphere, the organic sulfur compounds will decompose to yield sulfur dioxide. However, under the same condition, coal also will be oxidized and will lose heating value (Given and Wyss, 1961; Reid, 1958).

In summary, the organic sulfur and inorganic sulfur compounds behave quite differently during gas treatment. Reactions of pyrite are favored in an oxidizing atmosphere, while reactions of organic sulfur are favored in a hydrogen atmosphere. Most of the organic sulfur released during pyrolysis is in the form of volatile sulfur compounds that break away from the coal matrix. If it were not for the secondary fixation reactions between the volatile sulfur compounds and the carbonaceous material or ash components, most of the sulfur compounds should be removed at low temperatures. Before discussing the results of the experimental works, the previous work on coal desulfurization with gases will be discussed.

Review of Previous Work

Early interest in desulfurization using gas treatment concentrated mainly on the production of metallurgical coke. The various approaches can be categorized into pretreatment of the coal before carbonization, carbonization of the coal in various gases to remove sulfur compounds, or desulfurization of the coke to reduce sulfur content. Some successes were achieved, but no economically practical process is available. It was only in the late 60's when energy shortages first started, that interest turned to desulfurization of coal or char for use as a clean power plant fuel.

The gases used in the past to desulfurize coal include oxidizing gases (O_2, air and steam), reducing gases (H_2, NH_3, CO and hydrocarbon gases), inert gases (N_2 and He) and gas mixtures. Certain types of coal pretreatment and addition of chemicals were found to enhance desulfurization. This review divides the past work into desulfurization of coal and desulfurization of coke or char, depending upon the starting material used in the study.

Removal of sulfur from coal

Sulfur removal during conventional carbonization

When coal is carbonized, part of the sulfur in the coal is released in the gas product as volatile sulfur compounds. As the sulfur remaining in the solid product greatly influences the quality of the coke, many studies have been made on the behavior and removal of sulfur during carbonization processes.

Powell (1920a, 1921) made a systematic study of the reactions of coal sulfur in the coking process. The conclusions he obtained from studies of various coals were: 1) Decomposition of the pyrites to ferrous sulfide, pyrrhotite and hydrogen sulfide started at 300 °C, and reached a maximum between 400 °C and 600 °C; 2) the reduction of sulfate to sulfide was completed at 500 °C; 3) one-third to one-fourth of the organic sulfur decomposed to form hydrogen sulfide, with the primary decomposition being most active below 500 °C; 4) some organic sulfur formed volatile organic sulfur compounds and was retained in the tar; 5) some sulfur apparently recombined with the carbon, with this reaction being most active at 500 °C and higher. He also stated that there were secondary reactions between decomposition products such as hydrogen, hydrogen sulfide, volatile matter and the solid. These reactions might effect the sulfur removal.

Foerster and Geissler (1922) expressed a different view

from that of Powell. They carbonized a bituminous coal at 500 °C and 1000 °C and concluded that the pyrites and sulfates were only about half decomposed at 500 °C. The volatile sulfur came mostly from the inorganic compounds, and the organic sulfur content remained practically constant. Wibaut and Stoffel (1919) found that only 40-50% of the organic sulfur was removed by coking. In a latter paper, Wibaut (1922) concluded that part of the organic sulfur remaining in the coke was present in solid solution or held by physical adsorption and the remainder of the sulfur was retained by chemical bonding. This view supported the work by Powell (1923a,b) who made a study on the phase equilibrium between sulfur and carbon and concluded that the organic sulfur appeared as adsorbed free sulfur and solid solution.

Thiessen (1935) found from analyses of 82 samples that the relationship between the sulfur in coke (Sc) and the pyritic (Sp) and organic sulfur (So) in the original coal was:

$$Sc = 0.62Sp + 0.45So$$

Lowry et al. (1942), in making a statistical study of the results of the United States Bureau of Mines-American Gas Association Carbonization Assay Tests, found a similar relationship between sulfur in the coke (Sc) and total sulfur in the original coal (St):

$$Sc = 0.084 + 0.759St$$

Powell (1945) analyzed the volatile sulfur compounds from a carbonizing chamber and stated that over 95 percent of the sulfur in the gas was in the form of hydrogen sulfide. Most of the remainder was present as carbon disulfide. Mercaptans, thiophenes and carbon oxysulfide were also found in trace amounts.

In a more recent study, Eaton et al. (1948) used radioactive tracers to determine the principal sources of sulfur in coke. On a typical, full-scale 16 hour coking run, neither organic nor pyritic sulfur was preferentially removed. They concluded that in order to produce low sulfur coke, coal low in total sulfur content must be used. The organic sulfur was evolved more rapidly during the first part of the carbonization period, while the pyritic sulfur evolution, after an initial dip, remained more or less constant until late in the coking run. The form of the sulfur in the original coal might influence the optimum coking period.

Desulfurization in the conventional carbonization process is not adequate for coal with a high sulfur content. To achieve a better elimination of sulfur, processes utilizing pretreatment of the coal or a carbonization in a controlled atmosphere should be employed.

Desulfurization in a controlled atmosphere Powell (1920b) passed hydrogen gas through the coking mass. He found that coal pyrites were decomposed at low temperature, with the decomposition being complete at 500 °C. There was little decomposition of organic sulfur to hydrogen sulfide below 500 °C, but it increased enormously from 500 °C to 1000 °C. The reaction of a hydrogen sulfide-hydrogen mixture with carbonaceous material was reversible. A large amount of sulfide sulfur was converted to a carbon-sulfur complex. He also tried carbonization in a gas mixture similar to coke oven gas (H_2 50%, CH_4 25%, CO 15%, CO_2 and air 10%). The reaction was slow and did not give the degree of desulfurization attained in hydrogen. At 1000 °C, a 90% reduction of sulfur could be achieved by using hydrogen alone. In a later study on the phase equilibrium between sulfur and carbon (1923a,b), he concluded that the sulfur should be removed as hydrogen sulfide in a hydrogen atmosphere, since it has the highest dissociation pressure of any sulfur form in the coke.

Snow (1932) studied the desulfurization of Illinois No. 6 coal in various gases. After heating the coal at 1000 °C for 4 hours, the percentage of sulfur eliminated was: with nitrogen, carbon dioxide, carbon monoxide, methane or ethane, 50 to 60%; water gas, 76%; anhydrous ammonia, 82%;

hydrogen, 87%. At 800 °C, steam removed 84% of the sulfur, while water gas with hydrochloric acid gave 72.5% sulfur elimination. Partial removal of pyrite by oxidation and leaching, followed by carbonization in hydrogen gave a sulfur elimination of 93%. He also indicated that 50% of the organic sulfur could be released by carbonization and some inorganic sulfur might be converted to organic sulfur. Rapid heating in hydrogen might avoid the fixation of sulfur by the coal and ash and would result in more sulfur removal. However, the coal fused quite extensively and a hard coke was formed.

Brewer and Ghosh (1949) investigated the desulfurization effect of ammonia and a hydrogen-nitrogen mixture on two Pennsylvania coals and Illinois No. 6 coal. They found that the sulfur removal was augmented by longer treatment with ammonia and was increased still further if the sample was crushed to a finer size before ammonia was added. There was an increased desulfurization when the temperature was raised from 700 °C to 800 °C. Above 800 °C the desulfurizing effect was not markedly changed. About 70% sulfur elimination was achieved at 800 °C upon treatment with ammonia for 5 hours. The desulfurizing action of hydrogen was less than that of ammonia, but greater than that of nitrogen alone. They explained that conditions during the tests at 800 °C were favorable for nearly complete decomposition of the ammonia

into nascent hydrogen and nascent nitrogen. Nascent hydrogen would be expected to react more completely than molecular hydrogen with the sulfur compounds and thus would reduce the amount of sulfur left in the coke. The sulfur compounds in the product gas varied with temperature and gas type. From 700 to 800 °C there was a pronounced increase in the hydrogen sulfide in the gas. The mercaptan sulfur showed a marked increase above 800 °C. Larger amounts of carbon oxysulfide and sulfur were formed in the residual gas during treatment with ammonia.

Jacobs and Mirkus (1958) studied the desulfurizing action of a mixture of steam, nitrogen and air on Illinois No. 6 coal in a fluidized carbonizer. They found that desulfurization was sensitive to the form of sulfur in the coal and the particle size (in the range of 14-200 mesh), but not to the steam or air content of the gas. Residence time was a very important factor in the first 8 minutes, but less important at longer times. Desulfurization also improved with increasing temperature up to 427 °C and was highest at superficial fluidizing gas velocities above 22.5 cm/sec. Above 427 °C additional sulfur removal was counteracted by gasification and attendant loss of char yield. Under good desulfurizing conditions, sulfate and pyritic sulfur were reduced approximately 80%, while organic sulfur was reduced

by only 10%. They indicated film diffusion might be the limiting step in the reaction kinetics. The organic sulfur content of the original coal is the critical factor in determining whether this process is feasible.

Blum and Cindea-Muntean (1961) studied low temperature desulfurization by oxidizing coal with a gas mixture of steam and air. They reported that the effect of coal particle size in the range of 0-3 mm was not pronounced. Temperature and steam-air ratio were critical to desulfurization. High ash content seemed to increase desulfurization and reduce loss by combustion. The best results were obtained under the following conditions: temperature, 380 °C; steam-air ratio, 85:15; air flow rate, 27 liter/hr. After one hour at these conditions, 90-95% of the sulfur was eliminated, while only 4-5% of the carbon was lost.

In later papers, Cindea-Muntean (1963a, 1963b) investigated the kinetics and mechanism of desulfurization with the steam and air mixture. He indicated that the oxidation of pyrite in coal was similar to the oxidation of pure pyrite, and the rate of this oxidation was not influenced by the large surrounding carbonaceous mass. The instantaneous rates of desulfurization for the pyrite in coal and pure pyrite reached maximum values 7 and 5 minutes after the beginning of the experiment, respectively. Decreasing the sulfur content from 2.62% to 1.79% resulted in a decrease of volatile matter

content from 42.7% to 22.6%. A high desulfurizing rate was accompanied by a high degassing rate. The sulfur removed was mostly pyritic sulfur. Organic sulfur was partially removed as hydrogen sulfide which was part of the volatile matter. He suggested that there were two distinct stages in the desulfurization process: 1) the first period consists essentially of the creation of an increased porosity and therefore a large accessible surface; 2) this is followed by a period of chemical attack comprising a chemical reaction between sulfur and the oxidizing agent and the growth of the accessible surface by gasification.

Černič-Simić (1962) studied the factors that influence the behavior of coal sulfur during carbonization in nitrogen, hydrogen, ammonia and steam for eight coal samples with different rank and composition. By adding calcium and iron compounds to the coal sample to increase its ash content, she found that the resulting coal retained more sulfur than the original coal after carbonization. She explained that compounds of calcium and iron could form sulfides during the process, and thus the sample retained more sulfur. The lower the rank of coal, the greater the portion of organic sulfur that was released during carbonization. When radioactive S^{35} was added to the coal in the form of FeS_2, it was found that part of the S^{35} was retained by coal after carbonization in the form of organic sulfur. The amount of S^{35} retained

as organic sulfur decreased with rank, while the amount of S^{35} retained as inorganic sulfur increased with rank. Therefore, high rank coals seemed less active in the fixation of sulfur. The amount of sulfur retained in coke also depended on the total sulfur present, which indicated a possible equilibrium of

$$RS + H_2 \rightleftarrows R + H_2S \ .$$

Hydrogen removed 15-48% of the inorganic sulfur at 900 °C; ammonia removed 8-48% at 600 °C, which was little different than nitrogen. Steam at 600 °C was the most effective desulfurizing agent for inorganic sulfur and removed 80-90% of the radioactive pyrite. Černič-Simić concluded that coal rank influences desulfurization since it affects the amount of volatile matter that carries sulfur away, the linkage of the organic sulfur in the coal molecule, and the capability of the organic portion of the coal to fix sulfur. The mineral matter in coal may fix sulfur and also serves as a catalyst or inhibitor for the formation of volatile sulfur compounds.

Vestal and co-workers (1971; Yergey et al., 1974) studied the kinetics of coal and pyrite desulfurization in both hydrogen and oxygen containing atmospheres using non-isothermal experiments. The solid sample was heated in a reactor at a controlled rate with gases flowing over it.

The composition of the gases leaving the reactor was monitored continuously by a quadrapole mass spectrometer. The results showed the temperature at which adsorption, desorption and chemical reaction of various species occurred and the extent of the reactions. The data also were analyzed to obtain the values of the rate constant, activation energy, frequency factor and reaction order of the different reactions. The kinetic parameters for the principal hydrosulfurization reactions are reproduced in Table 2.

Three types of organic sulfur were observed and they

Table 2. Kinetic parameters for hydrodesulfurization reactions

Reaction	Order[a]	k_o[b]	E/kcal/mole
$(org.S)_I + H_2 \rightarrow H_2S$	1	3.1×10^{10}	34.5
$(org.S)_{II} + H_2 \rightarrow H_2S$	1	2.8×10^{11}	41.5
$(org.S)_I + (org.S)_{II} + H_2 \rightarrow H_2S$	1	2.0×10^{6}	22.0
$(org.S)_{III} + H_2 \rightarrow H_2S$	2	2.5×10^{7}	56.1
$FeS_2 + H_2 \rightarrow FeS + H_2S$	$\frac{1}{2}$	1.3×10^{11}	42.1
$FeS + H_2 \rightarrow Fe + H_2S$	1	9.7×10^{8}	43.1
$char + H_2S \rightarrow (C\text{-}S) + H_2$	1	2.3×10^{8}	32.0
$Fe + H_2S \rightarrow FeS + H_2$	1	6.5×10^{4}	18.0
$CaO + H_2S \rightarrow CaS + H_2O$	1	4.7×10^{13}	38.0

[a]Reaction orders with respect to sulfur species.

[b]Frequency factor, units depend upon reaction order.

evolved hydrogen sulfide at 380 °C, 430 °C and 470 °C, respectively. No effort was made to identify these sulfur compounds. Pyrite was observed to react with hydrogen in two stages with peaks at 495 °C and 560 °C. Hydrogen sulfide was observed to react rapidly with both iron and carbon.

Upon subjecting the sample to an oxidizing atmosphere, it was observed that pyrite adsorbed oxygen strongly at 210 °C and 560 °C and released sulfur dioxide at 530 °C and 560 °C. The evolution of sulfur dioxide at 530 °C seemed to be related to the oxygen adsorption at 210 °C, which indicated that the SO_2 evolution from pyrite occurred by two parallel processes. The evolution of sulfur dioxide from the organic sulfur compounds occurred at 350 °C, 480 °C, and 780 °C.

Sinha and Walker (1972a, 1972b) studied the desulfurization of seven United States coals by air oxidation at 350-450 °C. They concluded that temperature was the principal factor determining the extent of desulfurization. The efficiency of sulfur removal was controlled by the diffusion of oxygen into the coal and its pyrite. More than 90% of the pyritic sulfur could be removed at 450 °C in 10 minutes. However, 8-16% of the calorific value was lost due to the release of volatile matter and partial

oxidation of the coal. The sulfur dioxide concentration in the effluent gas had no effect on the desulfurization rate up to a concentration of 10%. A comparison between air, nitrogen, carbon monoxide and a steam-carbon monoxide mixture as desulfurizing gases in the temperature range 400-600 °C showed the order of desulfurizing ability to be: air>steam-CO mixture>CO>N_2.

Maa et al. (1975) investigated the transformation and removal of sulfur from western Kentucky coals in both nitrogen and hydrogen atmospheres. They found at low temperatures that the char sulfur content remained constant at 2.6% independent of the hydrogen sulfide concentration in the gas. However, the inhibition effect of hydrogen sulfide was pronounced at high temperatures. In pure hydrogen, sulfur removal increased continuously from 47% at 600 °C to 84% at 870 °C. In a nitrogen atmosphere, sulfur removal was 40% at 600 °C and increased to 59% at 740 °C. No further removal occurred above this temperature. The form of the sulfur at different temperatures was also reported. In a hydrogen atmosphere, sulfate sulfur increased with temperature, reaching a maximum at 500 °C, and then decreased to about 1% of the total sulfur in the original coal at 1000 °C. The organic sulfur decreased slightly at about 200 °C and then continued to decrease following a sigmoid curve to 4% at 1000 °C. Pyritic sulfur

started to decompose thermally to sulfide sulfur at 300 °C and was completely decomposed and reduced by hydrogen at 600 °C. Sulfide sulfur could not be removed completely until about 1000 °C. In a nitrogen stream, sulfate sulfur showed a maximum at 550 °C. Organic sulfur decreased slightly at 200 °C, then sharply at 600 °C, with no reduction of organic sulfur by pyrolysis being possible above 740 °C. Pyritic sulfur started to transform into sulfide sulfur at 300 °C and had almost completely disappeared at 740 °C. Sulfide sulfur could not be removed by heating at temperatures below 1000 °C.

Block et al. (1975) investigated the effect of air, steam and hydrogen on the desulfurization of 10 U.S. high-volatile bituminous coals. They found that air treatment at 450 °C removed 38% of the total sulfur, comprising 51% of the inorganic sulfur and 20% of the organic sulfur. With steam at 600 °C, 61% of the total sulfur, 87% of the inorganic and 25% of the organic, was lost. Hydrogen was not effective below 850 °C, but at 900 °C, 86% of the total sulfur was eliminated, 94% of the inorganic and 76% of the organic sulfur. They also reported that oxidative pretreatment at 300 °C for 10 minutes followed by treatment with hydrogen at 900 °C increased the desulfurization rate immensely.

Desulfurization with added chemicals Ghosh and Brewer (1950) studied the carbonization of a low-ash, good coking Indian coal which contained an abnormally high organic sulfur content. By adding sodium carbonate or lime, there was a moderate reduction of sulfur in the coke. On carbonization in ammonia gas at 800 °C, they found the low ash Indian coal caused less ammonia to be decomposed and had greater desulfurization than the three American coals with higher ash content. Tests were made by adding ferrous oxide or iron pyrite to the coal and a higher sulfur content coke was formed than without any addition. Increasing the percentage of ferrous oxide from 0.5% to 1% to 5% increased the sulfur content of the coke from 3.94% to 4.41% to 5.98%, respectively, as compared with 3.51% sulfur in the coke without added oxide. The addition of sand to the coal also increased the sulfur content. On the other hand, the addition of aluminum oxide in various percentages to the coal tended to reduce the sulfur content of the coke, especially when the carbonization with ammonia was extended over a long period or large amounts of aluminum oxide were added. They explained the high sulfur reduction by concluding that aluminum promoted decomposition of the ammonia and did not form stable aluminum sulfide.

Das (1948) found the sulfur content of coke formed from Ledo coal was reduced when 18% lime was added to the coal and the mixture was carbonized in thin layers at 1000 °C. The effect of lime addition is not clear as other workers observed that calcium oxide, calcium carbonate, dolomite and magnesium carbonate tended to retain more sulfur in the coke (Černič-Simić, 1962; Foerster and Geissler, 1922; Priestley and Cobb, 1928).

Priestley and Cobb (1928) found that addition of 5% iron oxide noticeably decreased the hydrogen sulfide evolution in an inert gas such as nitrogen, but had little effect upon the hydrogen sulfide evolution in hydrogen above 800 °C.

Lissner (1923) stated that addition of 5 to 10% iron improved the desulfurization by hydrogen.

Chowdhury et al. (1952a, 1952b) investigated the desulfurization of a high organic sulfur Assam coal. By treatment with a mixture of steam and air at 250-500 °C for 12-16 hours, 56.5-58.2% of the sulfur was removed. Treatment with moist ammonia for 10-15 hours at 650-800 °C removed 79-88% of the sulfur. Carbonization of coal pretreated with chlorides of sodium, magnesium, zinc and tin removed 62, 77, 81 and 62 percent, respectively, of the sulfur from the coal. Sodium bicarbonate was the most effective agent and removed 83-92% of the sulfur from the

coal. They reported that the sulfur compounds evolved during carbonization contained hydrogen sulfide, mercaptans, carbon disulfide and thiophene.

Roy and Gosawami (1953a, 1953b) studied the effect of inorganic catalysts on the desulfurization of Assam coal. The inorganic catalysts tested were silica, sodium silicate in jelly form, hydrated aluminum and bauxite. Silica appeared to be the best desulfurizing agent. Using a stream of steam, the sulfur content of coal was reduced 89% with a coke yield of 42% when the coal was carbonized with 5% silica at 850 °C for 6 hours. Using coal gas alone, carbonization at 800 °C for 6 hours reduced the sulfur from 4.57% in the coal to 1.97% in the coke product. Using 5% silica under the same conditions, the sulfur in the coke was reduced to 1.51%. In coal gas, calcium oxide gave a maximum desulfurization of 54%; magnesium chloride and aluminum oxide yielded coke containing 1.69 and 1.41% sulfur, respectively.

Batchelor et al. (1960a, 1960b, 1960c) have patented a process to desulfurize coal in an inert gas by adding a hydrogen sulfide acceptor containing magnesium oxide. Lee and Schorra (1972) patented a process for treating a mixture of equal volumes of coal and calcined limestone with hydrogen at 600-800 °C. They claimed essentially all the pyritic sulfur and 34% of the organic sulfur could be

removed by this process.

Given and Jones (1966) investigated the desulfurizing effect of 27 additives during carbonization. Addition of ammonium chloride, sodium borohydride, p-terphenyl (Santo wax P) and benzene-1,2,4,5-tetra-carboxylic dianhydride achieved higher sulfur reduction than carbonization without additives. They indicated that some volatile sulfur compounds were fixed by the organic matter in coal and this process occurred at 350-500 °C. If the sulfur content of the char is to be reduced, some additive is required which can interfere with this sulfur fixation process in the low temperature range. For effective action, the additive should be able to volatilize and penetrate the coal particles or diffuse readily through the fused mass. They also suggested that if finely divided coal were fluidized at 500-600 °C in a gas containing a fair partial pressure of ammonia, hydrogen or possibly moist carbon dioxide, it would likely achieve high sulfur reduction.

Removal of sulfur from coke or char

Monkhouse and Cobb (1922) reported a 94% removal of the sulfur from coke by passing hydrogen gas over the material at 1000 °C. The same extent of sulfur elimination was achieved by using a mixture of hydrogen and steam at 800 °C.

Pexton and Cobb (1923) desulfurized coke in the

temperature range of 800-1000 °C with a steam-nitrogen mixture. Their work showed that, at low carbon burn-off, steam was an effective desulfurizing agent for sulfide sulfur but not for organic sulfur.

Gurarii (1931) studied the effect of temperature (800-1200 °C) and particle size (2-15 mm) on the removal of sulfur from coke in steam and hydrogen. The efficiency of sulfur removal increased with increasing temperature and decreasing particle size.

Sabott (1952) desulfurized petroleum coke with gases at elevated temperatures. When ammonia gas was passed through hot coke, 28% of the sulfur was removed. When treated with unsaturated hydrocarbon gases such as ethylene, propylene and 2-butene at about 1500 °F, more than 90% of the sulfur originally present in the coke was removed.

Zielke et al. (1954) made a systematic study of the effect of total pressure (1-6 atm.), gas composition (0.1-1.0 hydrogen mole fraction) and carbon burnoff (0-40%) on the desulfurization of char at 871 °C in a fluidized bed with hydrogen and steam mixtures used as the fluidizing gas. Desulfurization increased with increases in the hydrogen-steam ratio. Pressure had no effect for pure hydrogen, but when a gas mixture was used sulfur removal increased with higher total pressure. At a given carbon burnoff, pure hydrogen was a better desulfurizing agent than

hydrogen-steam mixtures. When 13% methane was introduced into hydrogen, desulfurization was achieved without concommitant carbon burnoff. They indicated that the dependence of the desulfurization rate on hydrogen pressure was quantitatively similar to the methanation of char and these two processes were independent of each other. Sulfide sulfur was more readily removed than organic sulfur. They also introduced various fractions of hydrogen sulfide into the inlet gas to study its inhibition effect. They reported that hydrogen sulfide was not a strong inhibitor for the sulfide sulfur, but it was a strong inhibitor for the removal of organic sulfur. A hydrogen sulfide concentration of the order of 0.2% in the outlet gas caused a decrease in the relative desulfurization rate of the order of 10-40% depending upon the conditions employed. The relative desulfurization rate also decreased strongly with increasing percent carbon gasified. A sulfur elimination of 90% could be achieved with less than 20% carbon burnoff.

Blayden (1958) reviewed the desulfurization of coke and concluded that using a reducing gas would be expensive and it would be impossible to use lump coke.

Mason (1959) studied the desulfurization of petroleum coke in hydrogen at atmospheric pressure. Sulfur removal improved with increasing hydrogen flow rate; however, even with 1500 volumes of hydrogen per volume of coke per hour,

only half of the sulfur was removed at 705 °C in a 5.5 hour period. Hydrodesulfurization was greatly improved by pre-oxidizing the coke at low temperatures. With the optimum pre-oxidizing condition of 343 °C (91-94% coal recovery) followed by 2 hours hydrotreatment at 760 °C, a 1% sulfur coke was produced from a coke originally containing 7% sulfur. When a higher hydrogen pressure (3.5 atm.) was used, coke with 1% sulfur was obtained in periods of 30 minutes to 1 hour.

Šef (1960) studied the desulfurization of petroleum coke during calcination. He found that sulfur elimination decreased rapidly with increasing particle size up to 0.6 mm. Further increase in particle size had a comparatively small effect on desulfurization. Sulfur removal increased with pressure in the range 1-6.5 atm., but did not have a significant effect at higher pressures. Increasing the space-velocity had an effect on desulfurization similar to that of increasing pressure; little improvement was achieved by increasing gas velocity higher than 6 liter/gm coke-hr. A plot of sulfur removed versus yield of coke gave a smooth line which indicated that, other conditions being equal, the amount of sulfur removed depended only on the percentage of carbon gasified and not on the pressure and gas space-velocity used. A sulfur removal of 93.6% was reported under the best condition.

Batchelor et al. (1960d) studied the inhibition effect of hydrogen sulfide on the desulfurization of a low temperature char. Hydrogen premixed with various concentrations of hydrogen sulfide was introduced into the system to establish the equilibrium distribution of sulfur in gas and solid. They also used this "inhibition isotherm" to obtain a design equation for sulfur removal. They concluded that sulfur elimination is roughly a first order reaction independent of the sulfur level of the feed char:

$$- \frac{dS}{dt} = KP_{H_2}S \ .$$

However, in a continuous system, the "equilibrium" was exceeded. This result, along with the fact that high hydrogen pressure caused less inhibition, indicated the "inhibition isotherm" was not a true thermodynamic equilibrium. The net rate of desulfurization was determined by the competition between two processes, thermal fixation of the sulfur to produce a more stable form and its rate of removal by hydrogen while in the labile form. Thermal fixation occurred more rapidly the higher the temperature, which was also true for the hydrodesulfurization reaction. Thus, an optimum operating temperature was possible. For atmospheric pressure, this temperature was about 788 °C.

Mahmoud et al. (1968) studied the desulfurization of petroleum coke in hydrogen. Desulfurization was greatly

influenced by the temperature and particle size. The hydrogen flow rate also influenced the reaction rate. Over 90% desulfurization was obtained when 0.375 mm particles were treated at 600 °C for 40 hours.

Gray et al. (1970) hydrodesulfurized Illinois No. 6 coal char which contained 2% organic sulfur and 1% ferrous sulfide at 871 °C. Removal of the organic sulfur was rapid. The reaction of ferrous sulfide and hydrogen proceeded more slowly than would be expected from equilibrium. This was contrary to the findings of Zielke et al. (1954). There was barely any effect when particle size (28-200 mesh) and hydrogen space-velocity were varied. Higher pressure increased the rate of desulfurization to some degree. They concluded that because of the high pseudo-equilibrium ratio of hydrogen to hydrogen sulfide, it would require a vast amount of hydrogen to reduce the sulfur content in coke below 1%. Some hydrogen sulfide acceptor such as calcium oxide would have to be admixed with the char bed to have a commercially viable process.

Robinson and Green (1974) removed some of the iron and calcium salts by physical separation followed by a leaching of the coal with hydrochloric acid at 80 °C for about 5 minutes and demonstrated that the resulting coal char had a much reduced "inhibition isotherm". Thus, it is possible to reduce the sulfur content in char below 1% without

employing great quantities of hydrogen. This finding was consistent with the work of Snow (1932) who increased sulfur elimination by leaching coal with a boiling solution of ferric ammonium sulfate and sulfuric acid for 24 hours before treating with hydrogen at high temperature. The result also confirmed the work of Černič-Simić (1962) who stated that iron and calcium compounds tended to prevent the release of organic sulfur as volatile sulfur compounds as these formed sulfides and were retained in the product.

Factors that influence desulfurization

Summarizing the results of previous investigators, desulfurization is influenced by the following factors: type of gas, type of coal, temperature, particle size, gas flow rate and pressure, residence time and pretreatment or additives to the coal. The gas atmosphere determines the chemical reactions involved in desulfurization. In general, oxidizing gases are more effective for inorganic sulfur, while reducing gases are more effective for organic sulfur and inert gases are the least effective. The type of coal affects desulfurization in various ways. The total amount of sulfur and form of sulfur in the coal determines the difficulty and extent of desulfurization. As was discussed by Given and Wyss (1961) in their study of the chemistry of

inorganic and organic sulfur in coal, most of the sulfur compounds would be removed at low temperature if it were not for the fixation reactions with the carbonaceous material and ash components. The fixation of sulfur by the carbonaceous material consists of two processes; at low temperatures (250-500 °C), volatile sulfur compounds react with coal, while at high temperatures (600 °C and up) hydrogen sulfide reacts with coal and ash components. The fixation of sulfur in oxidizing atmospheres is not as serious as in reducing atmospheres as demonstrated by Sinha and Walker (1972a). The type of chemical bonding in the carbonaceous material in coal also determines the ease of release of the volatile sulfur compounds and their capability of recombining with it. Ash components can cause more sulfur to be retained in the solid product or may serve as catalysts or inhibitors for the formation of volatile sulfur compounds. The pretreatment or addition of chemicals to the coal essentially changes the properties of coal to achieve better sulfur removal.

Desulfurization is improved by decreasing the particle size, raising the temperature and increasing the gas flow rate, gas pressure and residence time. However, there is not enough kinetic information to predict either the rate or the extent of reaction. Further research in this field is needed.

Experimental

Apparatus and material

The apparatus used in the study of desulfurization was the same Rigaku thermal analyzer used in the study of devolatilization. However, because of the size of the sample holder, the coal sample weight was limited to 30 mg. The amount of solid residue remaining after the experiment with this size sample was too small for a statistically significant sulfur analysis. It was therefore necessary to modify the original system in order to handle a larger sample.

The modified system used the preprogrammed heating unit, temperature controlling system and data recording unit of the existing system. The only part that was changed was the sample holder. A platinum sample pan having a diameter of 10 mm and a depth of 5 mm and capable of holding 300 mg of coal sample was used. This sample pan was placed on a platinum heat pick-up plate which was supported by a quartz tube (4 mm inside diameter, 162 mm length). A chromel-alumel thermocouple was attached to the bottom of the heat pick-up plate to measure the temperature of the sample, with thermocouple wires passing through the center of the quartz tube. The quartz tube was plugged into a microbalance. The whole sample holder unit was confined in a quartz chamber 20 mm in diameter inside the high-power

electric heater. The gas flow was introduced from the bottom of the reaction chamber and was controlled by a rotameter and manually operated valves. During the experiment, the weight and temperature of the sample were recorded continuously. The sample holder unit is shown in Figure 19, and the set-up of the reaction chamber is shown in Figure 20.

The coal sample used came from the Jude mine, Mahaska County, Iowa, and is classified as a high volatile C bituminous coal. The analyses of the coal sample are shown in Table 3.

Table 3. Analysis of Jude coal

Proximate analysis	As received
Moisture	1.22
Ash	18.80
Volatile matter	39.68
Fixed carbon	40.30
Ultimate analysis	**Dry, ash-free basis**
C	60.45
H	4.56
N	∿1
O	∿26
S (total)	7.76
S (organic)	3.75
S (inorganic)	4.01
Calorific value	25.9 MJ/K gm

Figure 19. The modified sample holder unit

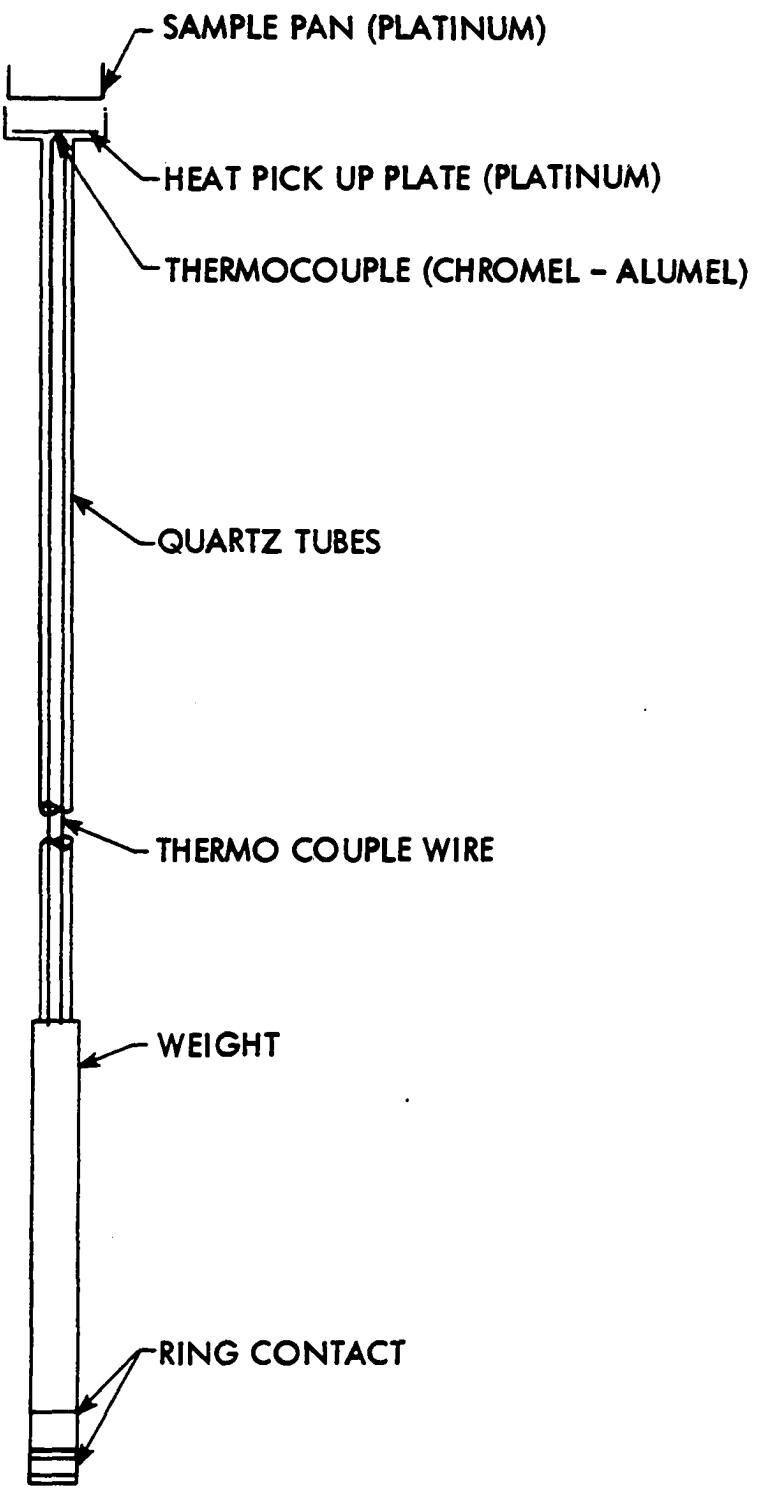
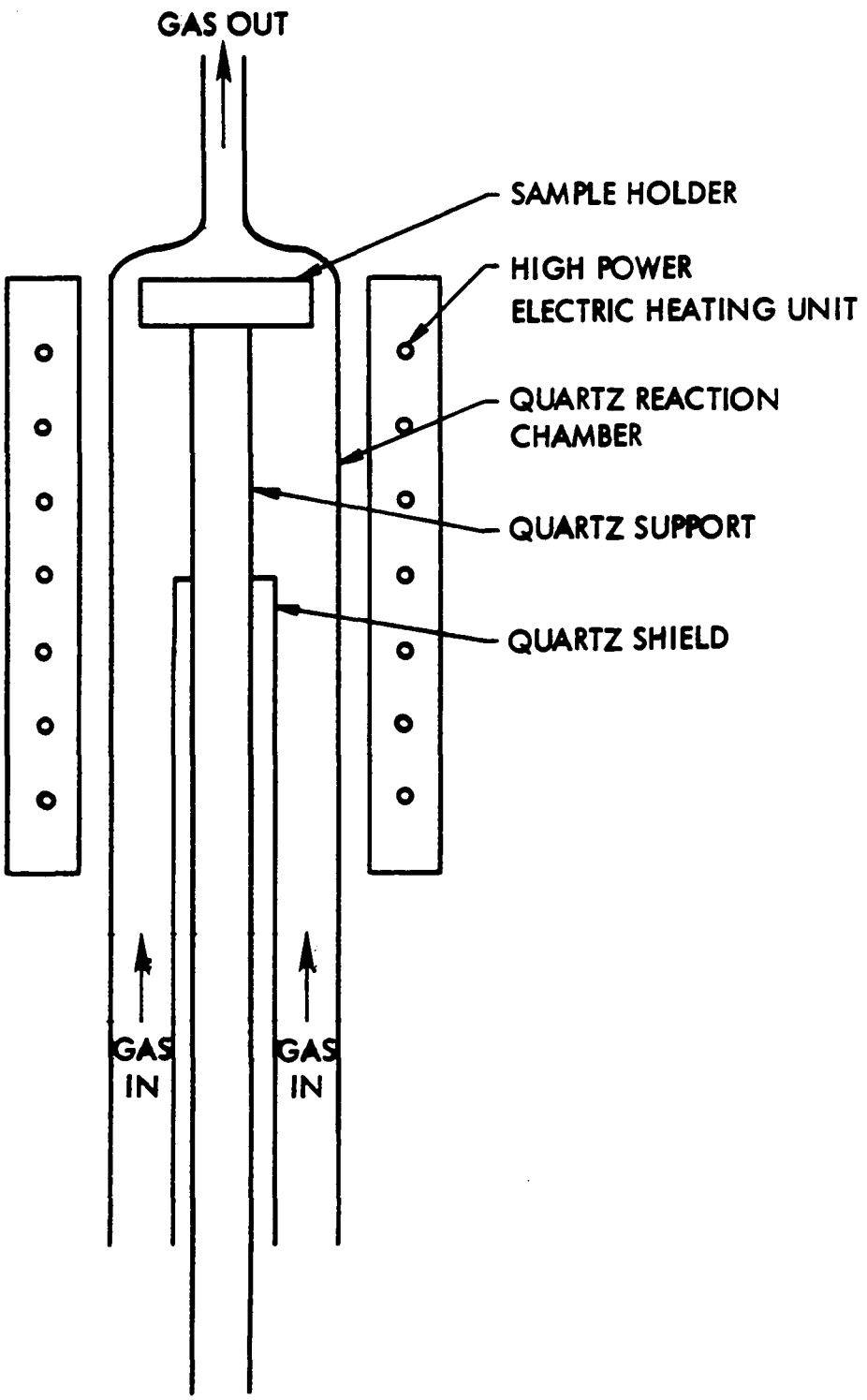

SAMPLE PAN (PLATINUM)
HEAT PICK UP PLATE (PLATINUM)
THERMOCOUPLE (CHROMEL - ALUMEL)
QUARTZ TUBES
THERMO COUPLE WIRE
WEIGHT
RING CONTACT

Figure 20. The reaction chamber set-up


GAS OUT
SAMPLE HOLDER
HIGH POWER
ELECTRIC HEATING UNIT
QUARTZ REACTION
CHAMBER
QUARTZ SUPPORT
QUARTZ SHIELD
GAS
IN
GAS
IN

Procedure

The experimental procedure employed in the study of desulfurization was similar to that used in the study of devolatilization, except that a quenching procedure was used to assure a precise reaction period. To start a run, about 300 mg of coal (< 125 μ) was dried at 110 °C for over 24 hours to remove all the moisture and then was charged into the sample pan inside the reaction chamber. The gas valve was opened and the gas was allowed to flow until the flow rate became stable which required about 10 minutes. The gas flow rate for runs with nitrogen and oxygen-nitrogen mixtures was maintained at 0.8 liter/min. The flow rate for hydrogen runs was 1.2 liter/min. The heater then was turned on and the sample was heated to the desired temperature using a constant heating rate of 20 °C/min., and was held at this temperature for a predetermined period of time. After the experiment, the heater was turned off and the gas flow was switched to an inert gas nitrogen (except for the nitrogen runs where no switch was needed). At the same time, the outside of the reaction chamber was cooled with a stream of air. The initial cooling rate of the reaction chamber was as high as 250 °C/min., which provided an adequate quenching of the reaction. After the reaction chamber was cooled, the solid residue was discharged, weighed, and analyzed for sulfur.

Sulfur analysis

The solid residue remaining after an experiment was analyzed for both total sulfur and organic sulfur content by an oxygen-flask method (Ahmed and Whalley, 1972, 1974). About 100 mg of finely ground sample was held in an envelope of ashless filter paper; the envelope was supported in a wire mesh or spirally-wound wire "grate" suspended in the center of a 2-liter Erlenmeyer flask filled with oxygen. The wire was made of platinum or chromel. About 15 ml. of 5% hydrogen peroxide was placed in the flask and used as the adsorption solution. The envelope was electrically ignited. After combustion, the product gas was absorbed in the solution; the solution was then diluted with distilled water in a volumetric flask. The diluted solution was titrated with Arsenzao (III) (1,8-dihydroxynaphthalene-3, 6-0 disulphonic acid-2,7-bis((azo-2)-phenylarsonic acid), sodium salt) for total sulfur content. The organic sulfur content was determined by leaching the coal sample overnight in nitric acid (12.5% by volume); after being filtered, washed and dried, the sample was combusted using the oxygen-flask method. The resulting sulfur content was considered to be organic sulfur. This method is not the standard technique for sulfur analysis. However, it has been employed by other investigators (Block et al., 1975). The sulfur analysis for this experiment was done at the Ames Laboratory

USERDA. Two determinations were done for each sample; the difference between the two determinations was usually under .2-.3%.

Results and Discussion

Two samples of Jude coal were used in this study, the raw coal and a deashed coal. The raw coal contained 3.25% inorganic sulfur and 3.04% organic sulfur (moisture-free basis). The deashed coal was prepared by twice floating the raw coal in a heavy liquid medium of specific gravity 1.3 to remove some of the ash and inorganic sulfur. It contained 4.74% organic sulfur, but only 0.69% inorganic sulfur. Thus, the reaction of the deashed coal manifested largely the behavior of the organic sulfur compounds in the coal. The proximate analysis of the deashed Jude coal is shown in Table 4.

Table 4. Proximate analysis of deashed Jude coal

Moisture	2.21
Ash	5.54
Volatile matter	45.72
Fixed carbon	46.53
Calorific value	29.4 KJ/K gm

The effect of three different gas atmospheres was investigated in the experiments: nitrogen, hydrogen and a 6% oxygen - 94% nitrogen gas mixture. In nitrogen the temperature range studied was between 300 and 700 °C, with the holding time at the final temperature being under 40 minutes. The temperatures studied in hydrogen were also between 300 and 700 °C and the holding time was under 60 minutes. With the oxygen-nitrogen gas mixture, the temperature range used was between 350 and 455 °C, and the holding time was under 40 minutes. The experimental data taken at the different treatment conditions are tabulated in Appendix B. The results of the experiments are discussed in the following sections.

Results from typical run

To determine the amount of sulfur removed at any given temperature and holding time required one experimental run since the sample was treated under the desired conditions and then was analyzed for sulfur. The effect of both temperature at zero holding time and holding time at a given temperature were determined during the course of the experimental program. Each of these required a series of experimental runs either varying temperature at zero holding time or holding time at some constant final temperature.

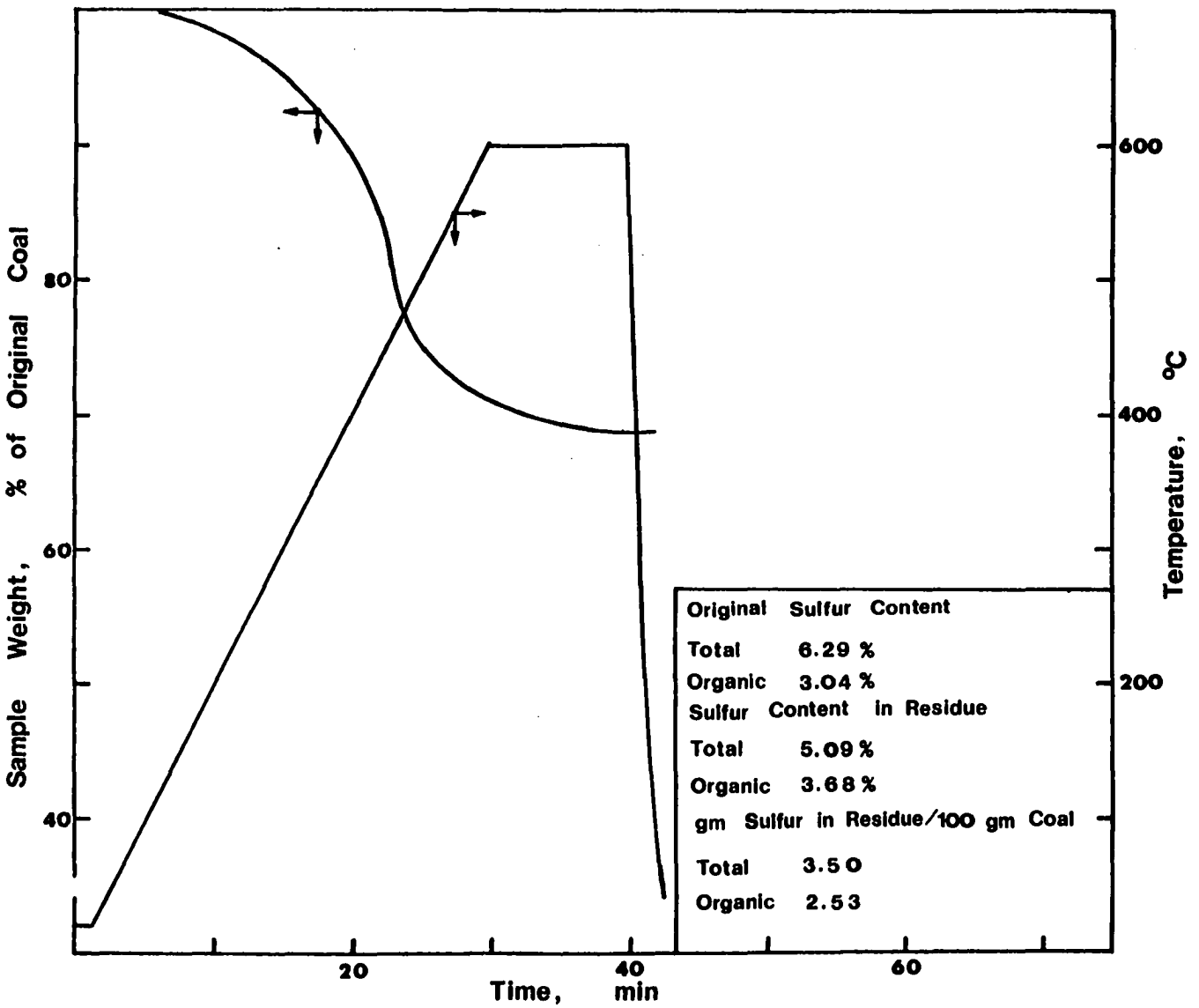
During each run, the temperature and sample weight were

recorded continuously. Typical temperature and sample weight versus time curves during the course of one experiment are shown in Figure 21. In this experiment, the coal sample was heated in a hydrogen atmosphere to 600 °C at a heating rate of 20 °C/min., and was held at 600 °C for 10 minutes before it was rapidly cooled to room temperature.

The weight versus time curves in different gas atmospheres differed from each other. In nitrogen, the weight loss was due solely to the devolatilization and this condition gave the smallest weight loss. During treatment with hydrogen, the weight loss was due to both devolatilization and hydrogasification and was larger than the loss in nitrogen. This difference increased as the final temperature or holding time increased. In the oxygen-nitrogen gas mixture the weight loss was due to devolatilization and oxidation and was the largest among the losses in the three gas atmospheres.

The sulfur content of the coal sample before and after the experiment is shown in the corner of Figure 21. In general, the sulfur contents of the solid residue after treatment in nitrogen for both the raw and deashed coal were in the range of 2.7 to 7.5%. The sulfur contents of the solid residue after treatment in hydrogen were in the range of 1.4 to 7%. Some solid residues after low temperature treatment had higher sulfur contents than the original

Figure 21. Temperature and sample weight versus time curves for a typical run


Sample Weight, % of Original Coal
80
60
40
20
40
60
Time, min
600
400
200
Temperature, °C
Original Sulfur Content
Total 6.29 %
Organic 3.04 %
Sulfur Content in Residue
Total 5.09 %
Organic 3.68 %
gm Sulfur in Residue/100 gm Coal
Total 3.50
Organic 2.53

coal sample. This shows that the evolution of carbonaceous material was greater than the removal of sulfur compounds at these low temperature conditions. The sulfur contents of the solid residue after treatment in the oxygen-nitrogen mixture were in the range of 2.8-5%. In order to compare the results at different treatment conditions, the sulfur contents for the different experiments were expressed in terms of the amount of sulfur per 100 gm of original coal sample. This was calculated using the following equation:

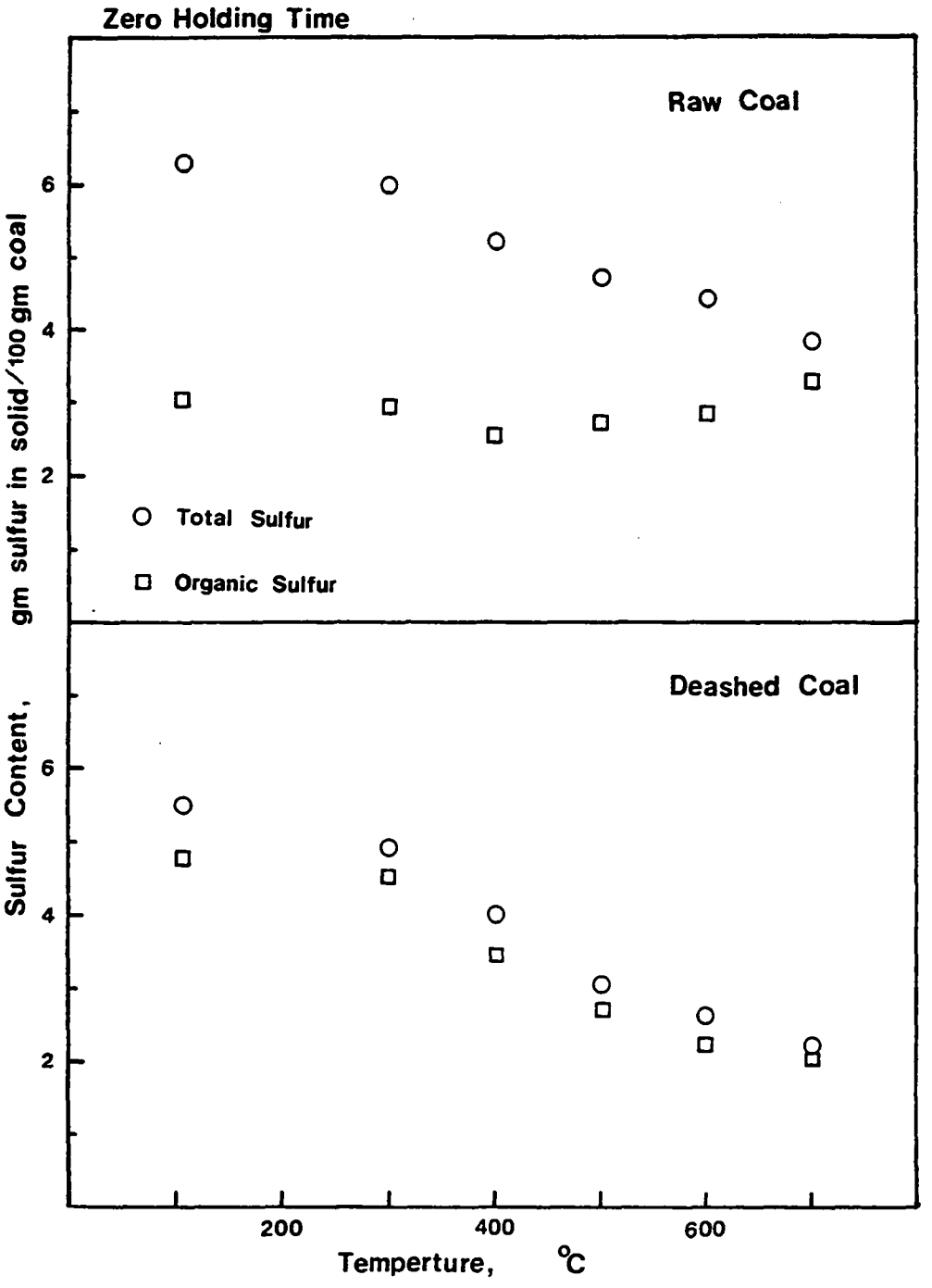
$$\text{sulfur content} = \text{sulfur content of the solid residue} \times \text{weight recovery} \times 100$$

Desulfurization in nitrogen atmospheres

Effect of temperature and holding time The sulfur content of a sample exposed to nitrogen depends on the treatment time and final temperature. Figure 22 shows the total sulfur and organic sulfur contents for both raw coal and deashed coal when treated in nitrogen atmospheres at different temperatures. In each case, the sample was not held at the final temperature, but was cooled immediately upon reaching this temperature (referred to as zero holding time).

The total sulfur content of deashed coal started to decrease at a temperature below 300 °C; it then followed a sigmoid curve with the most rapid decrease occurring between

Figure 22. The effect of temperature on the total sulfur and organic sulfur contents for both raw coal and deashed coal in nitrogen


Zero Holding Time
Raw Coal
Deashed Coal
Total Sulfur
Organic Sulfur
Sulfur Content, gm sulfur in solid/100 gm coal
2
4
6
200
400
600
Temperture, °C

300 and 500 °C and finally leveled off at higher temperatures. The total sulfur versus temperature curve for the raw coal followed essentially the same pattern, except the decrease was less rapid. At 700 °C, the total sulfur removal for the deashed coal was 60%, while the total sulfur removal for the raw coal was 40%.

Several runs were made to study the effect of holding time at the final temperature. Figures 23 and 24 show the total sulfur and organic sulfur contents versus time for both raw coal and deashed coal at 400 °C and 700 °C, respectively. For each experiment the coal sample was heated to the final temperature with a 20 °C/min. heating rate and was held at the final temperature for the desired period of time. At 400 °C, the sulfur contents reached an equilibrium value in about 15 minutes. At 700 °C, the equilibrium value was reached almost as soon as the final temperature was attained. This showed that the desulfurization reaction was taking place mostly during the heating period before reaching 700 °C.

Since there are no chemical reactions between nitrogen and the sulfur compounds in coal, the desulfurizing effect during heating in a nitrogen atmosphere is either due to the release of sulfur compounds as volatile matter or the reactions between the volatile matter and the sulfur compounds which free them from the solid phase. The temperature

Figure 23. The effect of holding time on total sulfur and organic sulfur contents for both raw coal and deashed coal with nitrogen treatment at 400 °C

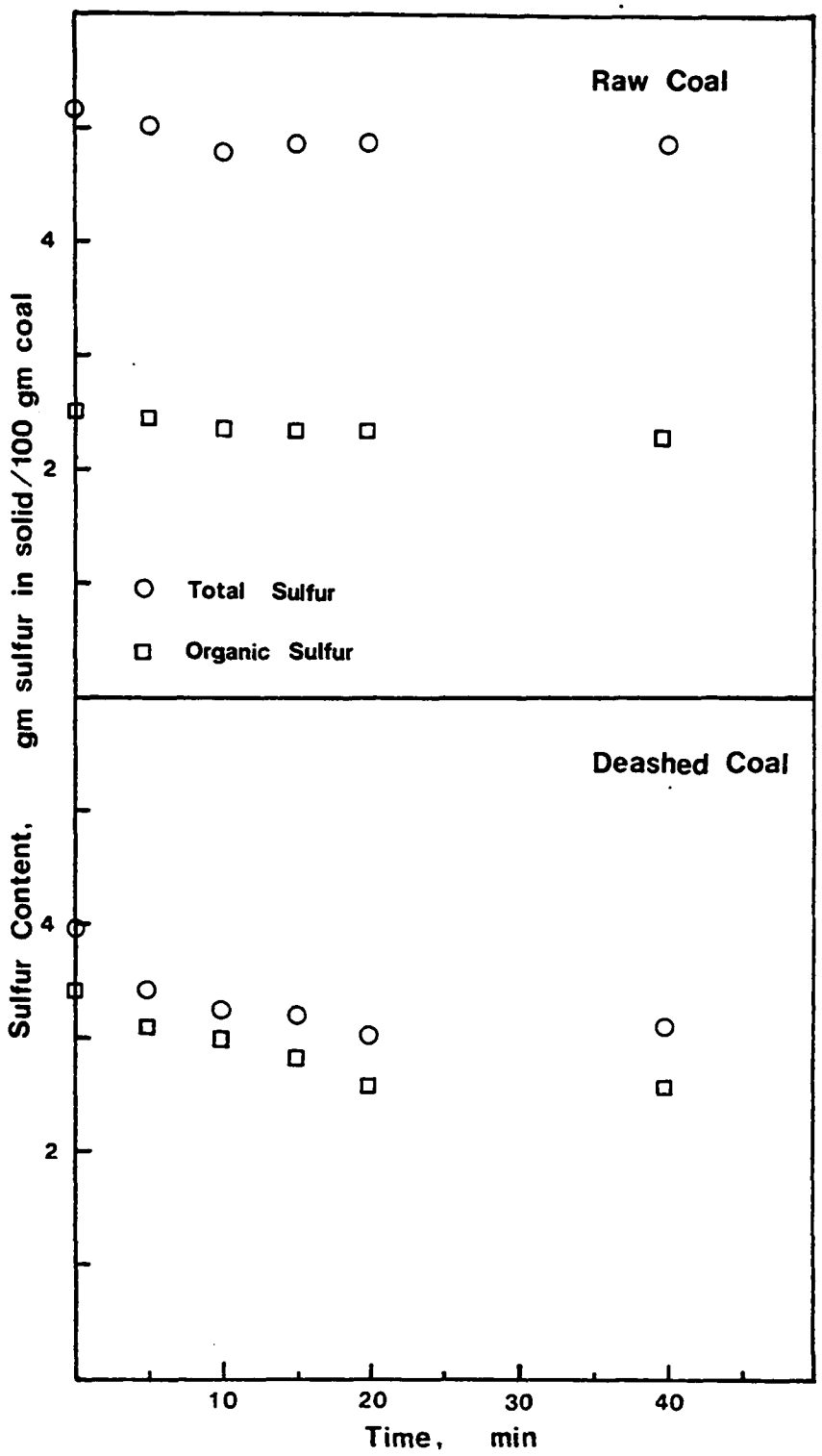
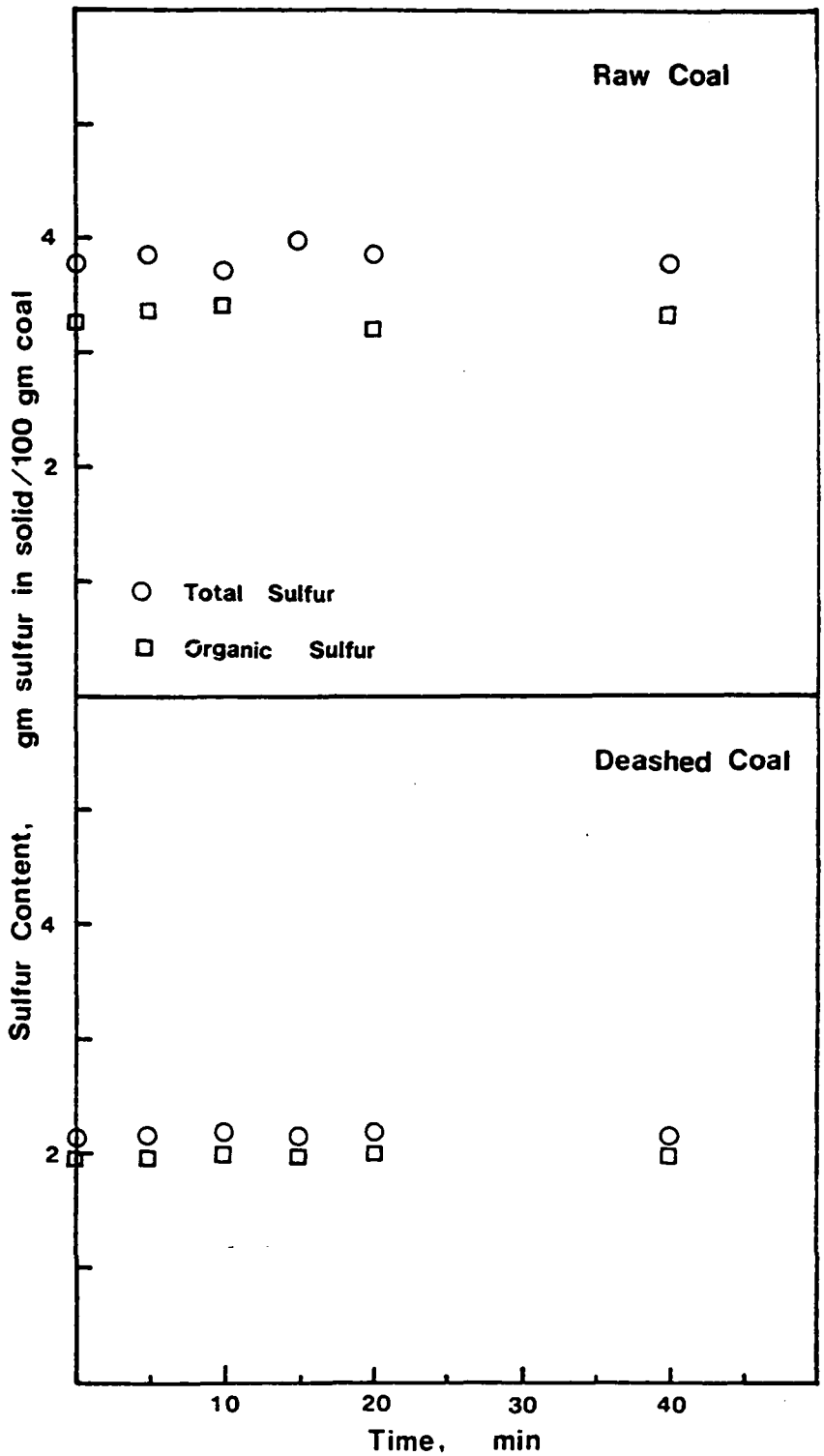

Raw Coal
Deashed Coal
Total Sulfur
Organic Sulfur
Sulfur Content, gm sulfur in solid/100 gm coal
4
2
4
2
10
20
30
40
Time, min

Figure 24. The effect of holding time on total sulfur and organic sulfur contents for both raw coal and deashed coal with nitrogen treatment at 700 °C


Raw Coal
Deashed Coal
Total Sulfur
Organic Sulfur
Sulfur Content, gm sulfur in solid/100 gm coal
2
4
2
4
10
20
30
40
Time, min

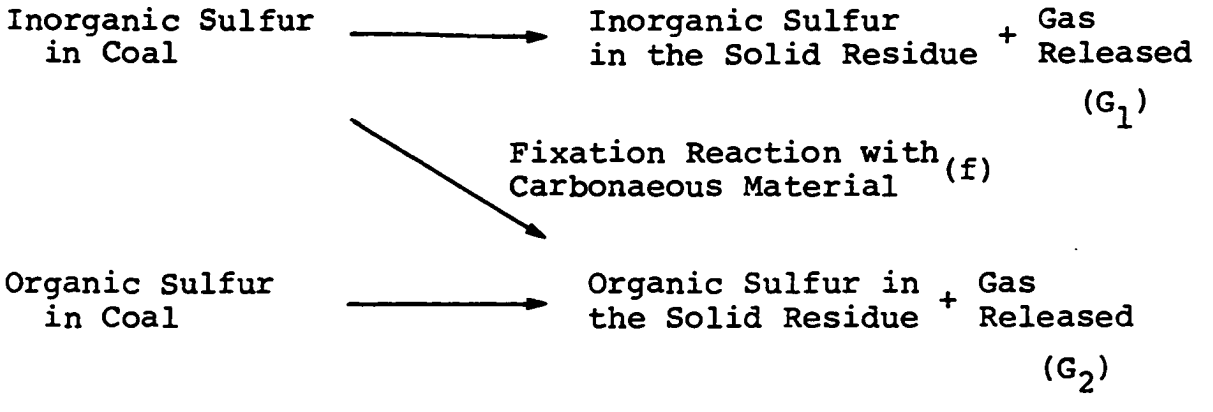
range from 300 to 500 °C, where the largest sulfur reduction occurred, is the plastic zone for coal where the primary decomposition dominates the devolatilization reaction. The initial period of constant temperature devolatilization also was dominated by the primary decomposition. It appears that the removal of sulfur compounds in nitrogen took place mainly during the primary decomposition period.

The reduction in inorganic sulfur was insignificant below 400 °C, but increased considerably between 400 and 700 °C. The holding time seemed to have little effect on the inorganic sulfur removal, as the inorganic sulfur content at a given temperature was almost unchanged for different holding times. At 700 °C, the equilibrium inorganic sulfur content of the raw coal had a mean value of 0.52% and a standard deviation of 0.12%; the mean sulfur content of the deashed coal was 0.18%, with a standard deviation of 0.04%. The raw coal contained about three times as much inorganic sulfur as the deashed coal. This is roughly the same ratio as that for the ash contents of these two coal samples (16-18%: 5-6%). The equilibrium inorganic sulfur content therefore appeared to be roughly proportional to the ash content of the coal sample.

Transformation of sulfur compounds in nitrogen atmospheres As was shown in Figure 22, the organic sulfur content of the raw coal started to decrease below 300 °C, reached a minimum at around 400 °C and then increased again; at 700 °C the organic sulfur content reached a level higher than the organic sulfur content of the original coal sample. However, this phenomenon was not observed with the deashed coal. The deashed coal, which originally contained 1.5 times more organic sulfur then the raw coal, had only 60% as much organic sulfur as the raw coal after treatment in nitrogen at 700 °C. Since the raw coal contained a substantial amount of inorganic sulfur, these results indicated that there was a transformation of inorganic sulfur during the treatment process.

The transformation of inorganic sulfur into organic sulfur also has been reported by other investigators. Snow reported that some inorganic sulfur might be converted to organic sulfur during carbonization. Mazumdar et al. (1959), Van Krevelen et al. (1959) and Ivengar et al. (1960) have all reported reactions between elemental sulfur and carbonaceous material at temperatures above 250 °C. Černič-Simić added radioactive S^{35} in the form of pyrite to coal and, after carbonization, the S^{35} was retained in the form of organic sulfur.

Experimental observations indicate that during the treatment process some of the inorganic sulfur is released as gas and some is transformed into organic sulfur. The organic sulfur compounds in the solid residue come from either the original inorganic or organic sulfur. It is of interest to calculate the fraction of inorganic sulfur released as gas (G_1) or transformed into organic sulfur (f), and the fraction of original organic sulfur compounds released as gases (G_2). If the reactions of both organic and inorganic sulfur compounds are assumed to be independent of the type of coal sample, the following reaction scheme applies to the raw coal as well as to the deashed coal.



The material balance for the sulfur compounds in the raw coal gives

$$(S_i^* - S_i) = fS_i^* + G_1 S_i^* \qquad \text{(inorganic sulfur)}$$

$$(S_o^* - S_o) = G_2 S_o^* - fS_i^* \qquad \text{(organic sulfur)}$$

The material balance for the sulfur compounds with the deashed coal gives

$$(\alpha S_i^* - S_i') = f\alpha S_i^* + G_1 \alpha S_i^* \quad \text{(inorganic sulfur)}$$

$$(\beta S_o^* - S_o') = G_2 \beta S_o^* - f\beta S_i^* \quad \text{(organic sulfur)}$$

Solution of the above equations leads to the following relationships,

$$f = \frac{\beta S_o - S_o'}{(\beta - \alpha) S_i^*} \tag{1}$$

$$G_1 = 1 - f - \frac{S_i}{S_i^*} \tag{2}$$

$$G_2 = 1 - \frac{S_o}{S_o^*} + f \frac{S_i^*}{S_o^*} \tag{3}$$

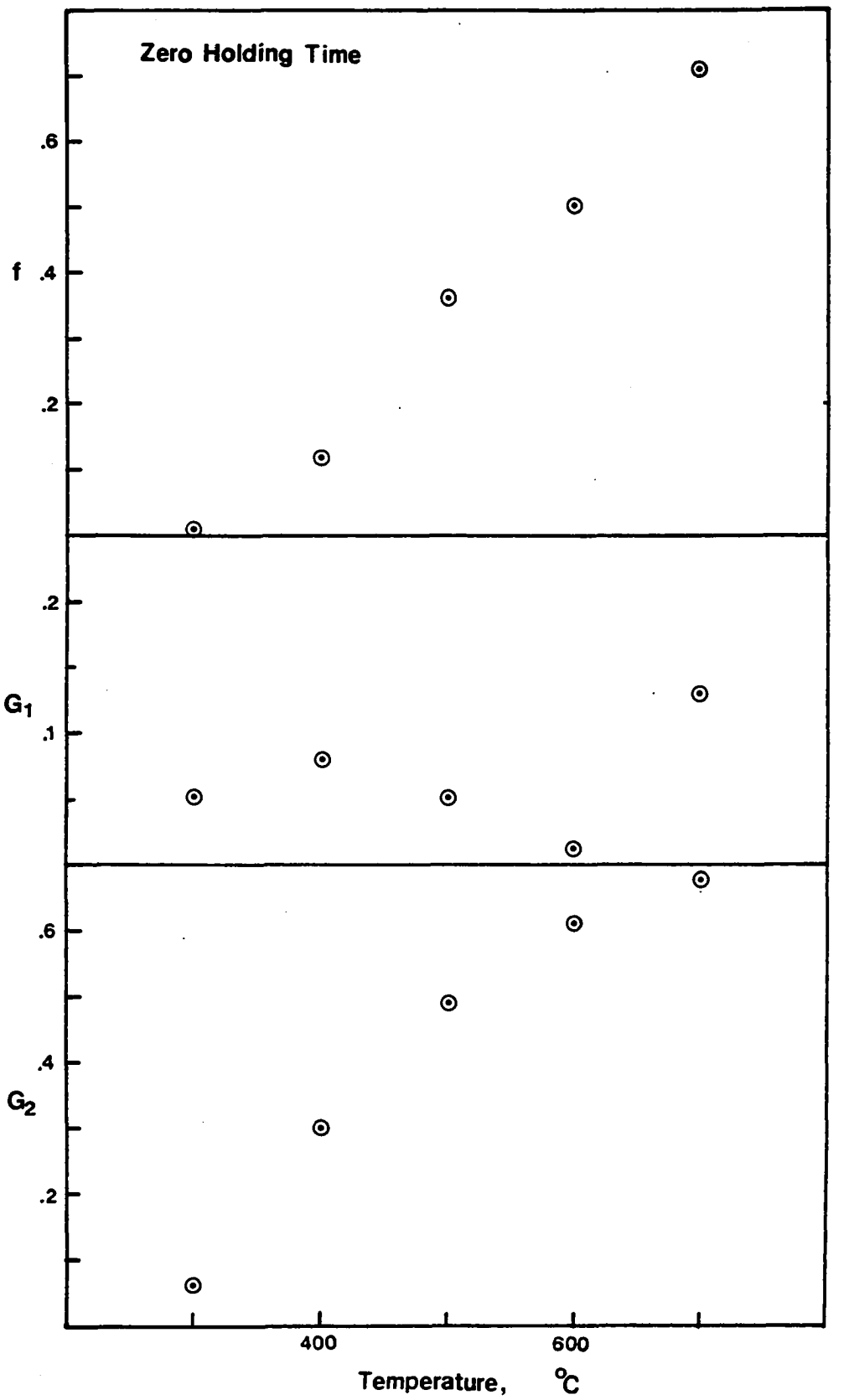
or

$$G_2 = 1 - \frac{S_o'}{\beta S_o^*} + f \frac{\alpha S_i^*}{\beta S_o^*} \tag{4}$$

These parameters at different temperatures and holding times can be calculated by inserting the experimental data for both raw coal and deashed coal at the treatment condition into the above equations. The calculated values and a sample calculation are shown in Appendix C.

Figure 25 shows the parameters calculated for the sulfur reaction scheme as a function of temperature (zero holding time). These values are obtained by inserting the

Figure 25. The effect of temperature on the parameters for the sulfur reaction scheme with nitrogen treatment


Zero Holding Time
f
.6
.4
.2
G_1
.2
.1
G_2
.6
.4
.2
400
600
Temperature, °C

numerical values from Figure 22 into equations (1)-(4). The fixation reaction, characterized by f, started at 300 °C and increased rapidly between 400 and 500 °C; the percentage of inorganic sulfur that reacted with the carbonaceous material and transformed into an organic form reached 70% at 700 °C. The fraction of inorganic sulfur released (G_1) was generally small. At 700 °C only about 12% of the original inorganic sulfur was released into the gas phase. The amount of organic sulfur released increased rapidly with temperature between 300 and 500 °C and then started to level off between 600 and 700 °C. About 70% of the original organic sulfur was released as gaseous compounds at 700 °C. This is the upper limit of desulfurization in nitrogen atmospheres at the treatment condition, providing that 100% of the inorganic sulfur has been separated from the coal.

The influence of holding time at the final temperature is less important. Figures 26 and 27 show these parameters versus reaction time at constant temperatures of 400 °C and 700 °C, respectively. These values are calculated by inserting the numerical values from Figures 23 and 24 into equations (1)-(4). The values of G_1 are generally small at both temperatures. Both f and G_2 increased slightly with holding time at 400 °C, but there was almost no effect of holding time at 700 °C. This indicated that the release

Figure 26. The effect of holding time on the parameters for sulfur reaction scheme with nitrogen treatment at 400 °C

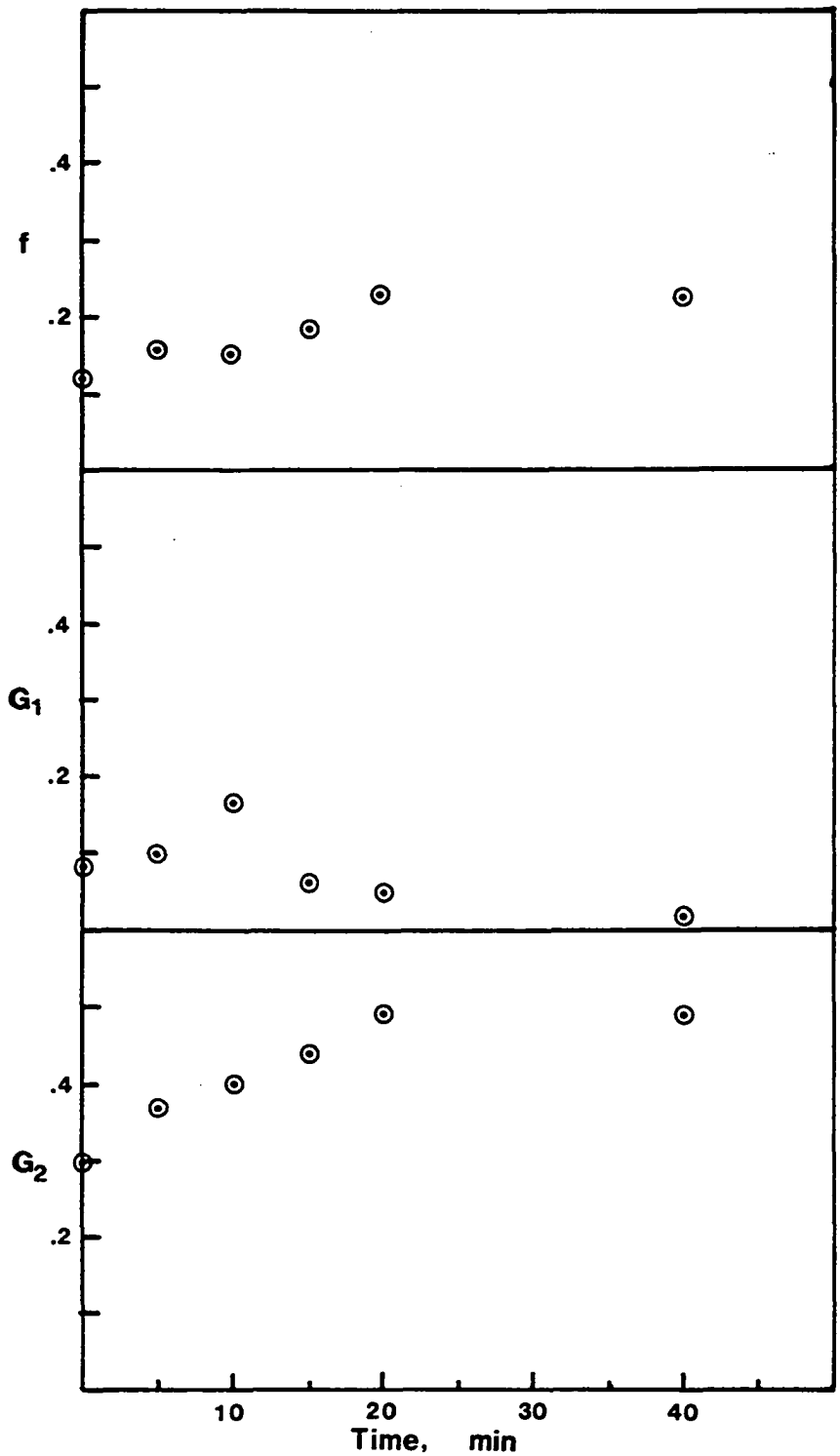
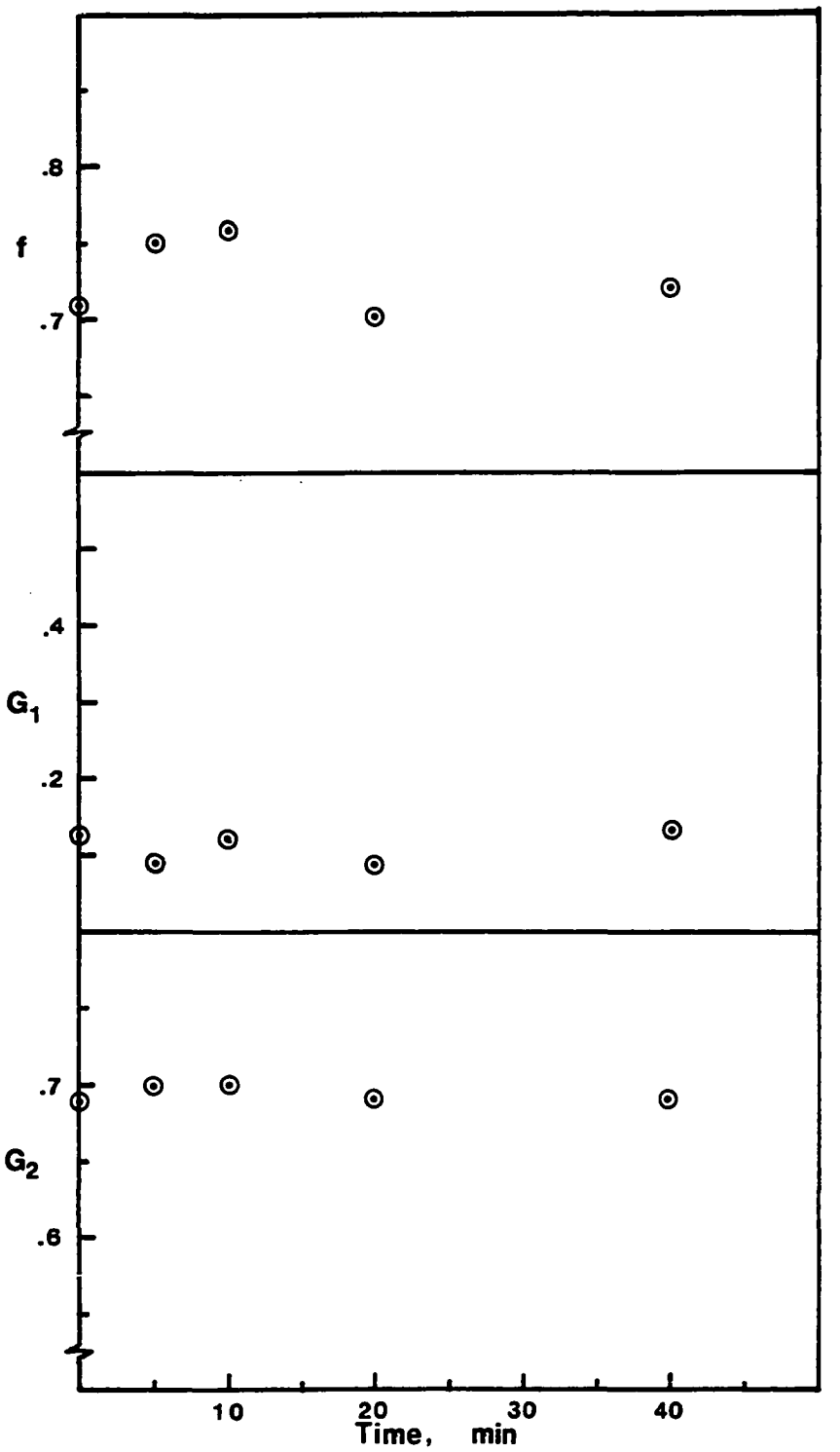

f
.4
.2
G_1
.4
.2
G_2
.4
.2
10
20
30
40
Time, min

Figure 27. The effect of holding time on the parameters for sulfur reaction scheme with nitrogen treatment at 700 °C


.8
f
.7
.4
G_1
.2
.7
G_2
.6
10
20
30
40
Time, min

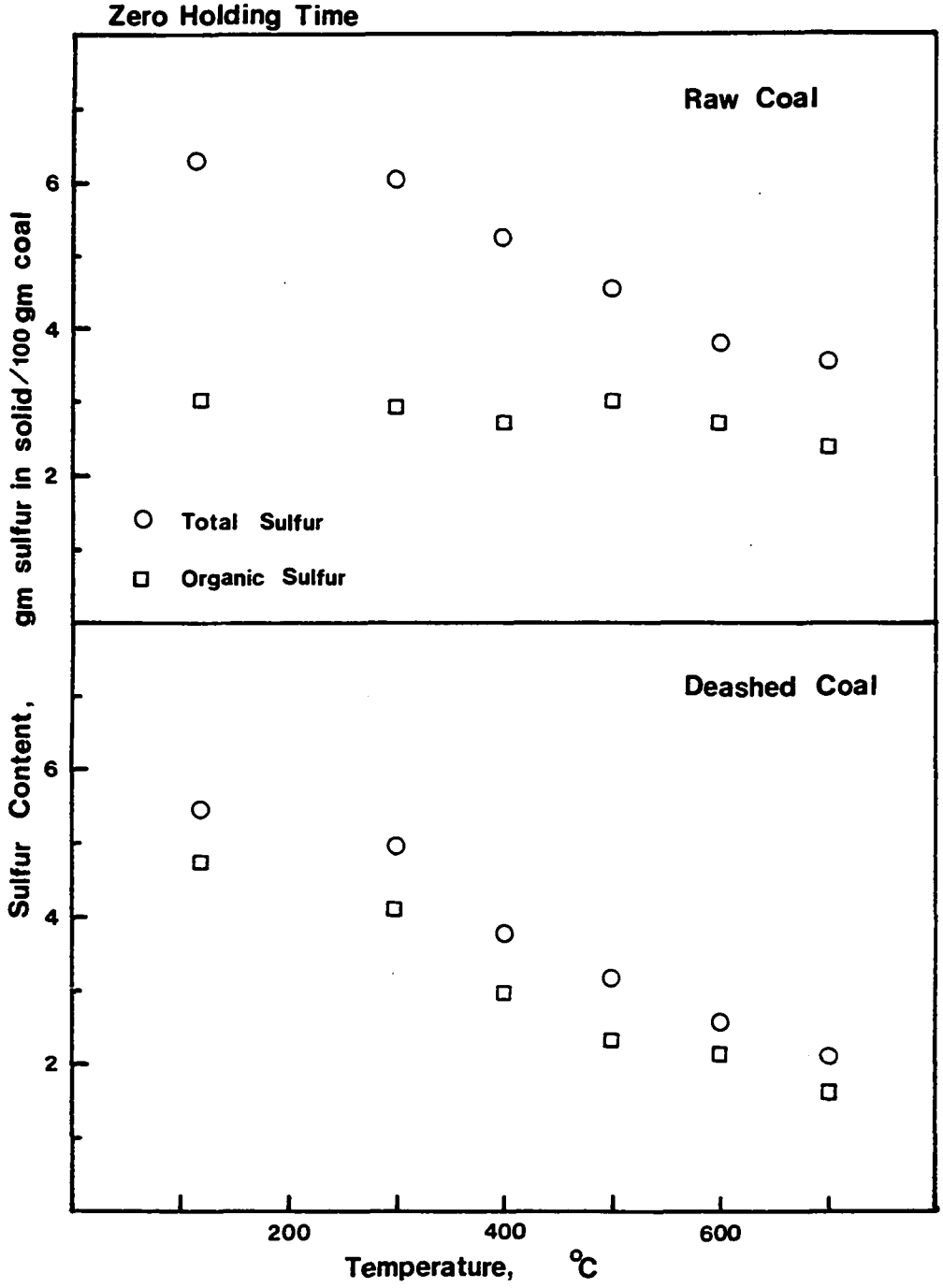
of organic sulfur compounds and the transformation of inorganic compounds took place mainly during the heating period before the temperature reached 700 °C.

Desulfurization in hydrogen atmospheres

Effect of temperature and holding time Figure 28 shows the total sulfur and organic sulfur content for both raw coal and deashed treated with hydrogen at different temperatures. The holding time at the final temperature was zero in each case. For deashed coal, the change in total sulfur content with temperature in hydrogen followed a trend similar to that for the total sulfur reduction in nitrogen. The organic sulfur reduction in hydrogen was consistently higher.

For raw coal, the sulfur contents with hydrogen treatment were not too much different than those with nitrogen at temperatures below 500 °C. However, there was a considerable improvement in the total sulfur reduction with hydrogen treatment at temperatures above 600 °C. The organic sulfur content of the raw coal treated in hydrogen went through a minimum around 400 °C and a maximum around 500 °C. The continuing increase of organic sulfur with temperature above 500 °C, as was observed in nitrogen, did not occur. However, the deashed coal, which originally contained 1.5 times more organic sulfur than the raw coal, had only half the

Figure 28. The effect of temperature on the total sulfur and organic sulfur contents for both raw coal and deashed coal in hydrogen


Zero Holding Time
Raw Coal
Deashed Coal
Total Sulfur
Organic Sulfur
Sulfur Content, gm sulfur in solid/100 gm coal
2
4
6
200
400
600
Temperature, °C

organic sulfur content of the raw coal after treatment with hydrogen at 700 °C. This indicated that the transformation of inorganic sulfur into organic sulfur also took place in hydrogen atmospheres.

Figures 29 and 30 show the sulfur contents of the raw coal and deashed coal at constant temperatures of 400 °C and 700 °C, respectively. The sulfur contents for both coal samples reached an equilibrium value in less than 20 minutes at 400 °C, but there was a continuing reduction of sulfur after one hour of treatment at 700 °C. This prolonged sulfur reduction, which did not occur in nitrogen at the same temperature, was due primarily to the direct hydrogenation of the sulfur compounds in the coal.

As discussed in the previous section, the amount of inorganic sulfur remaining in the solid after treatment with nitrogen at 700 °C was roughly proportional to the ash content of the coal sample. After hydrogen treatment at 700 °C, the raw coal contained about twice as much inorganic sulfur as the deashed coal. This ratio was smaller than the ratio of ash contents of these two coal samples. However, the equilibrium value of the inorganic sulfur content had not been reached after one hour of treatment. It is not certain therefore, whether the equilibrium inorganic sulfur content in hydrogen and the ash content of the coal sample are

Figure 29. The effect of holding time on total sulfur and organic sulfur contents for both raw coal and deashed coal with hydrogen treatment at 400 °C

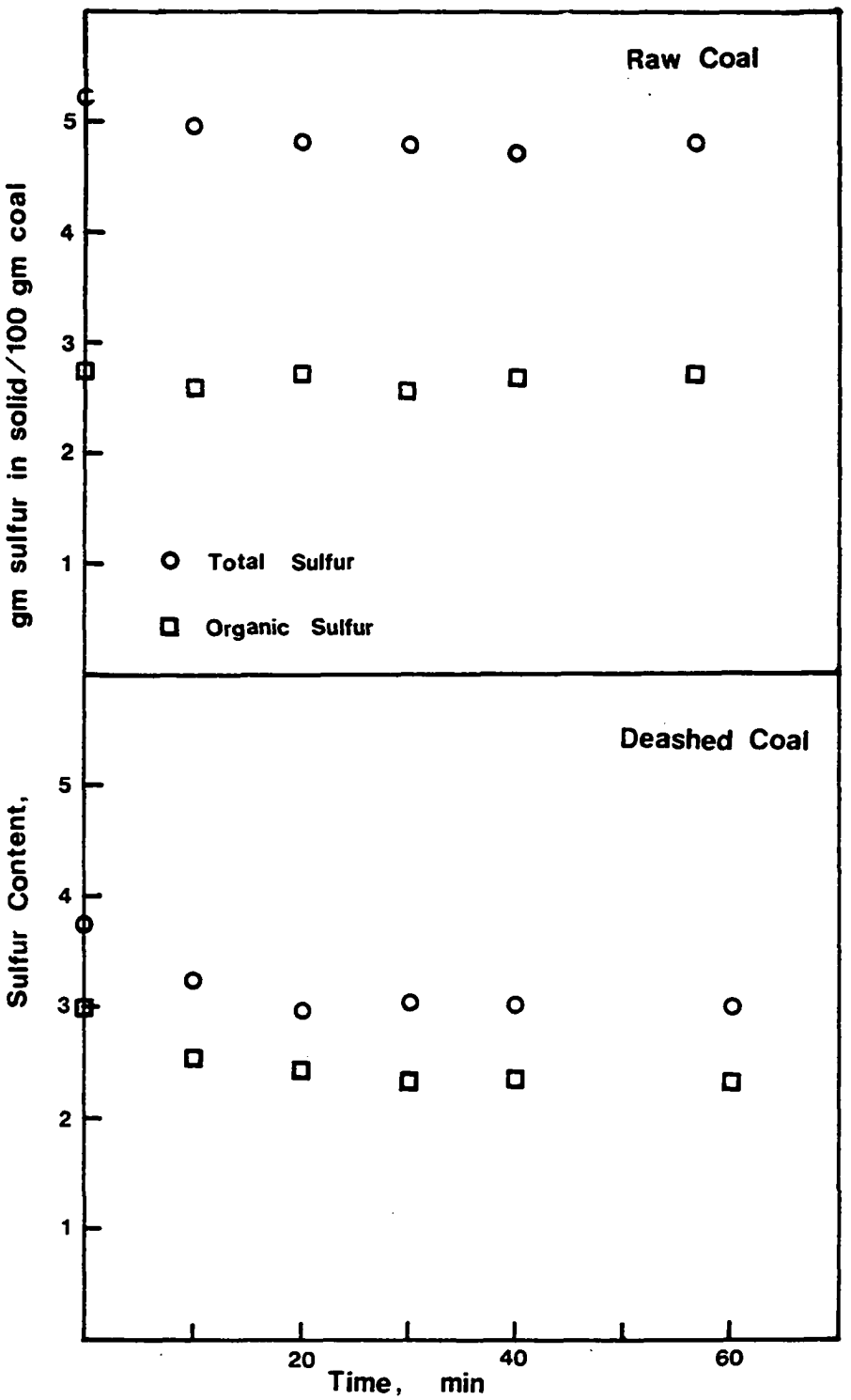
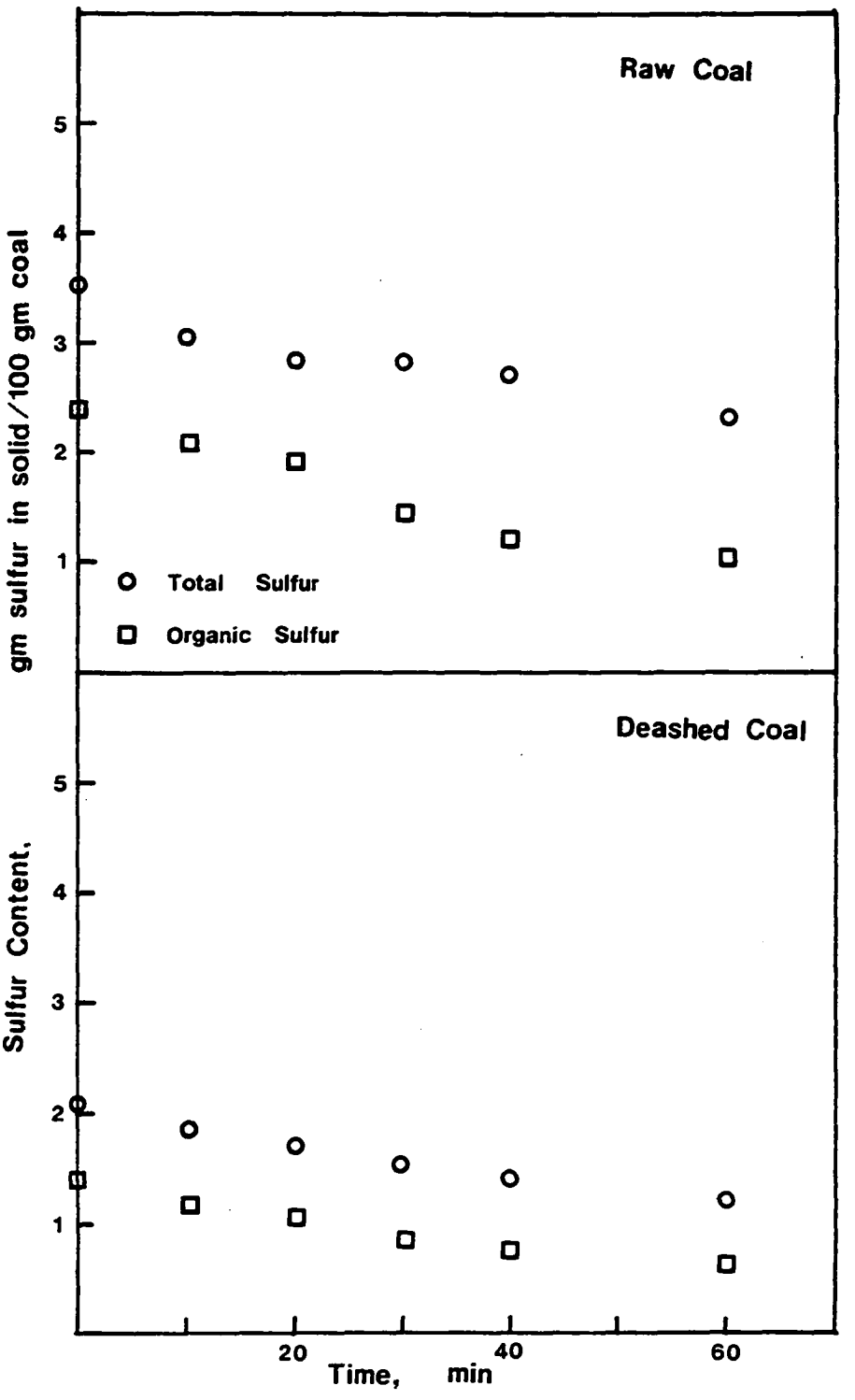

Raw Coal
Deashed Coal
gm sulfur in solid/100 gm coal
Sulfur Content,
Total Sulfur
Organic Sulfur
1
2
3
4
5
20
40
60
Time, min

Figure 30. The effect of holding time on total sulfur and organic sulfur contents for both raw coal and deashed coal with hydrogen treatment at 700 °C


Raw Coal
Deashed Coal
gm sulfur in solid/100 gm coal
Sulfur Content,
Total Sulfur
Organic Sulfur
1
2
3
4
5
20
40
60
Time, min

proportional.

Comparing the results of desulfurization in hydrogen and nitrogen atmospheres (Figures 22, 23, 24 versus Figures 28, 29, 30), the inorganic sulfur content after hydrogen treatment was consistently higher for the same temperature and treatment time. The reason for this is that the inorganic sulfur is in the sulfide form at temperatures above 400 °C. As has been shown on Figure 18, the equilibrium constant for the reaction

$$FeS + H_2 \rightleftarrows Fe + H_2S$$

is of the order of 10^{-5} to 10^{-2} in the temperature range of this experiment. The reverse reaction was thus favored thermodynamically. As a result, there was more inorganic sulfur retained with hydrogen. This reaction between iron in the ash and hydrogen sulfide has been reported by Batchelor et al. (1960d) and Yergey et al. (1974).

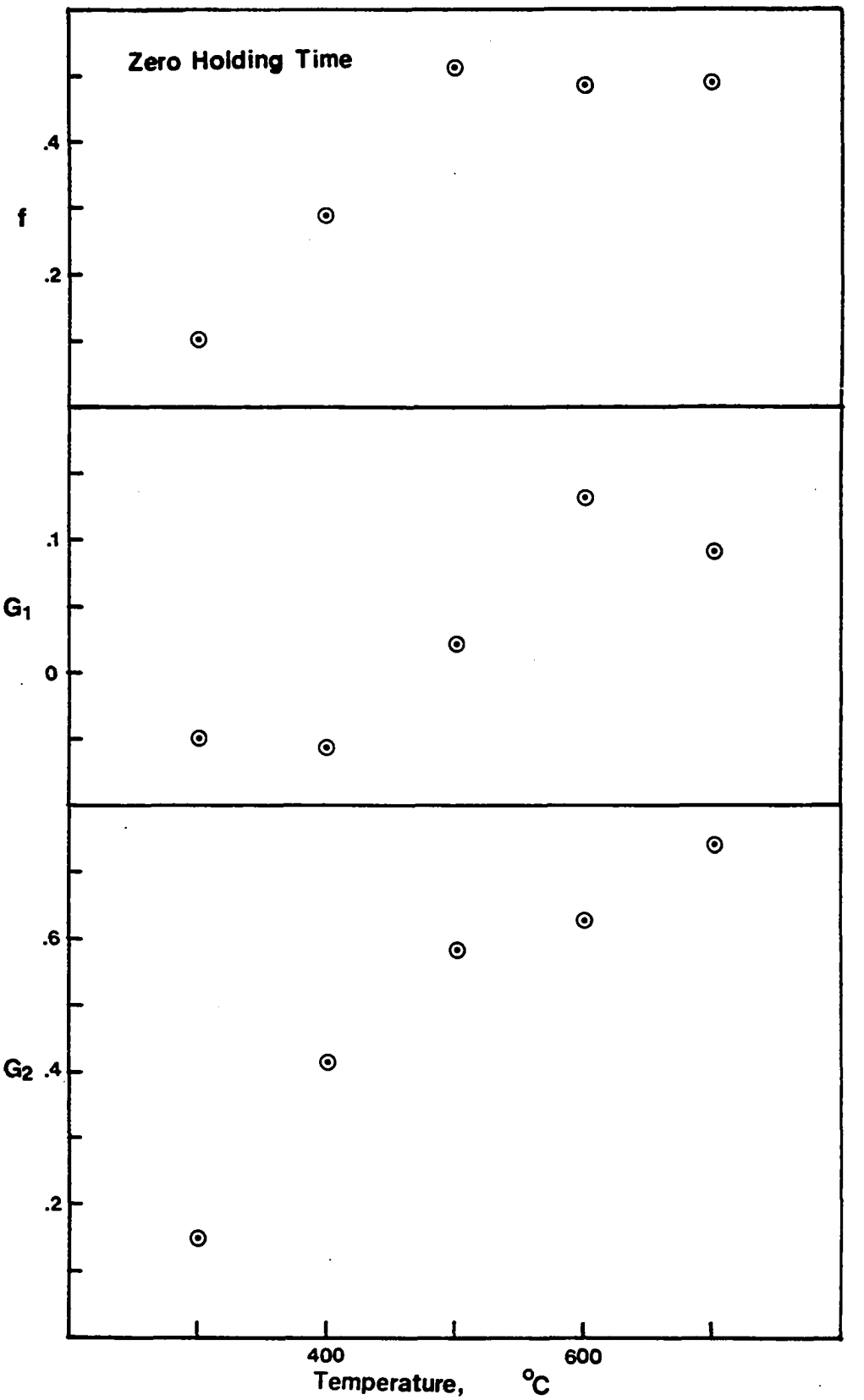
Transformation of sulfur compounds in hydrogen atmospheres The transformation of inorganic into organic sulfur that took place during treatment in nitrogen also happened during the hydrogen treatment. Moreover, because there were chemical reactions between the sulfur compounds and hydrogen, the whole reaction scheme was more complicated. The fixation reactions occurred not only between

sulfur compounds and the carbonaceous material, but also between sulfur compounds and the ash components.

The reaction scheme for sulfur compounds in coal proposed in the previous section also was applied to interpret the results from the desulfurization experiments in hydrogen atmospheres. Figure 31 shows the parameters calculated from the reaction scheme as a function of temperature using the data from Figure 28. The fraction of inorganic sulfur transformed into organic sulfur (f) was larger in hydrogen than in nitrogen at low temperatures. It reached a constant value of 0.5 at 400 °C and remained at this level at higher temperatures. This result was different from that in nitrogen, where the amount of inorganic sulfur transformed increased continuously up to 700 °C. It indicated that a reverse transformation of organic sulfur compounds into inorganic sulfur compounds was taking place in hydrogen that offset the forward transformation.

The fraction of inorganic sulfur released into the gas phase (G_1) was slightly negative at 300-400 °C, and increased to around 0.1 at 600-700 °C. The negative value of G_1 represents the fixation of volatile sulfur compounds to form inorganic sulfur. In fact, the values of G_1 at 400 °C were all between -0.05 and -0.08. As discussed in the previous section, the reaction, $Fe + H_2S \rightarrow FeS + H_2$, was favored thermodynamically. However, because of the

Figure 31. The effect of temperature on the parameters for the sulfur reaction scheme with hydrogen treatment


Zero Holding Time
f
.4
.2
G_1
.1
0
G_2
.6
.4
.2
400
600
Temperature, °C

small conversion of the inorganic sulfur, it is not certain if the above reaction was actually responsible for the results at this temperature.

The amount of organic sulfur released (G_2) increased with temperature and followed the same pattern as in nitrogen atmospheres. The amount of organic sulfur removed in hydrogen was about 10% higher than in nitrogen.

Figures 32 and 33 show the parameters versus holding time at constant temperatures of 400 °C and 700 °C, respectively. At 400 °C, the amount of inorganic sulfur transformed (f) and the amount of organic sulfur released (G_2) both increased with holding time. At 700 °C, the amount of inorganic sulfur transformed decreased continuously with holding time up to 60 minutes. This showed that organic sulfur was being transformed into inorganic sulfur and indicated that the reaction $Fe + H_2S \rightarrow FeS + H_2$ was taking place at this temperature. This result is consistent with the findings of Yergey et al. (1974), Černič-Simić (1962) and Robinson and Green (1974), who reported a reaction between hydrogen sulfide and the iron in the ash at high temperatures. The amount of organic sulfur released at 700 °C increased as the holding time increased. About 90% of the organic sulfur in the original coal sample could be removed by treating the sample in hydrogen at 700 °C for one hour.

Figure 32. The effect of holding time on the parameters for the sulfur reaction scheme with hydrogen treatment at 400 °C

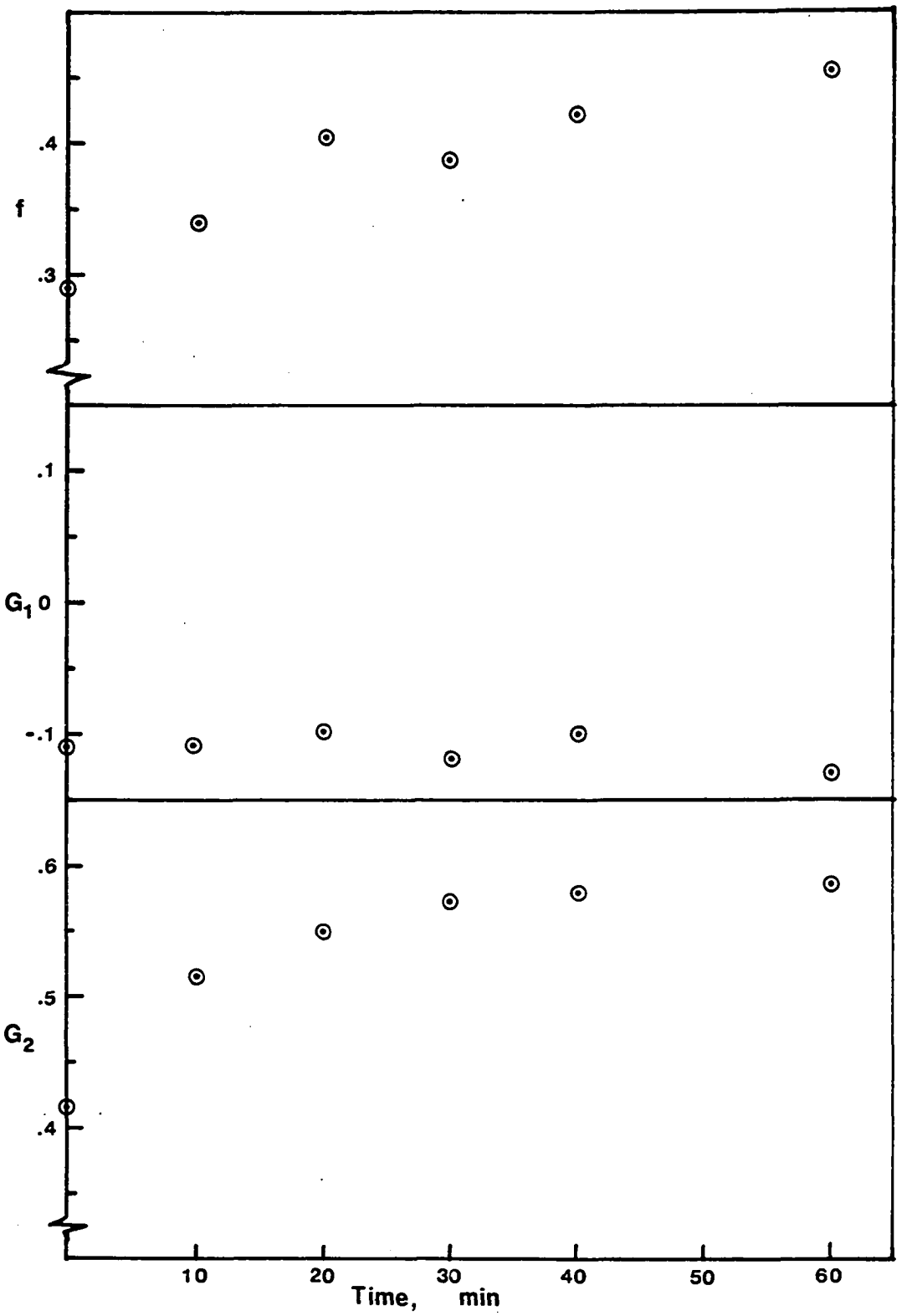
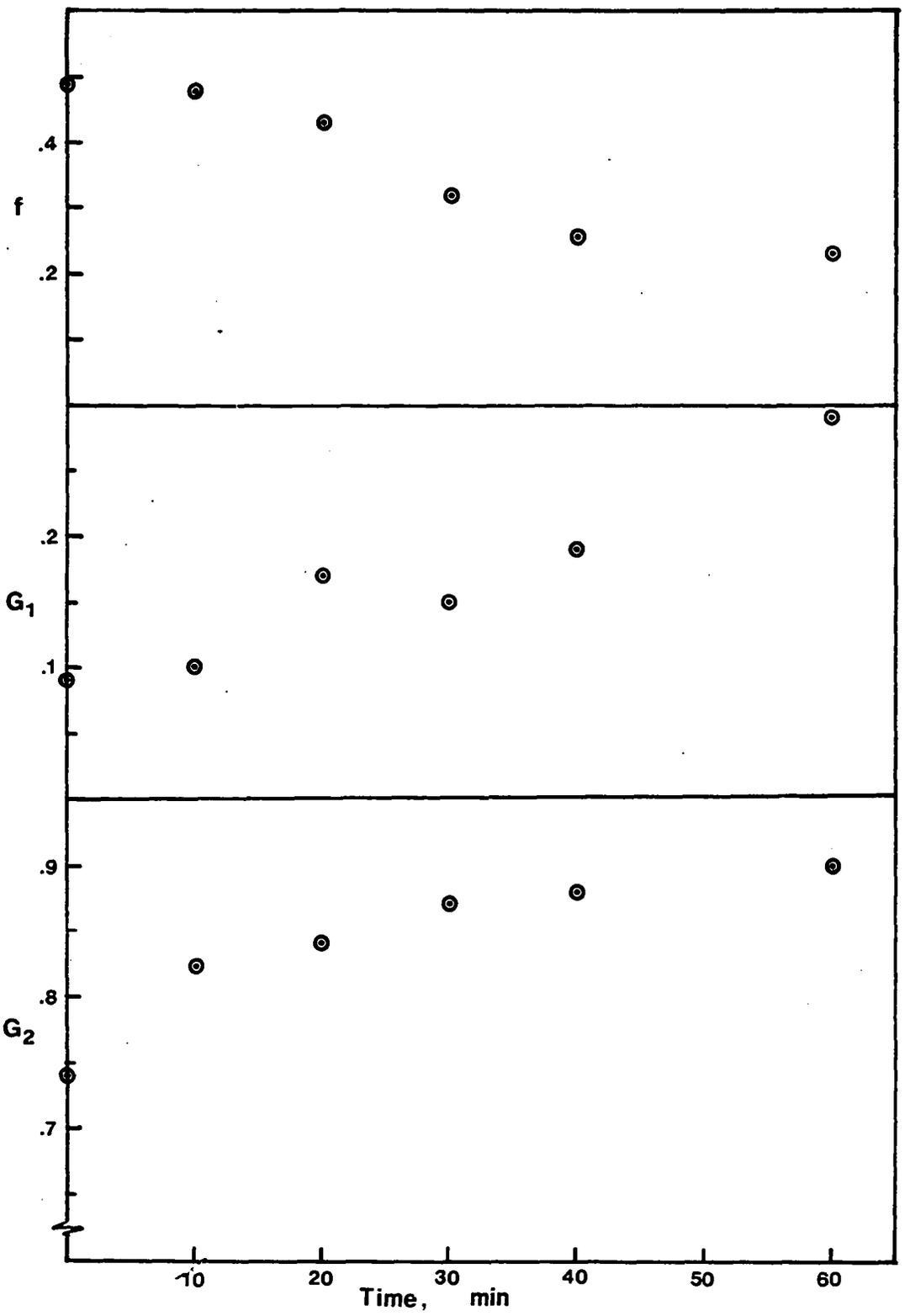

f
.4
.3
G_1 0
.1
-.1
G_2
.6
.5
.4
10
20
30
40
50
60
Time, min

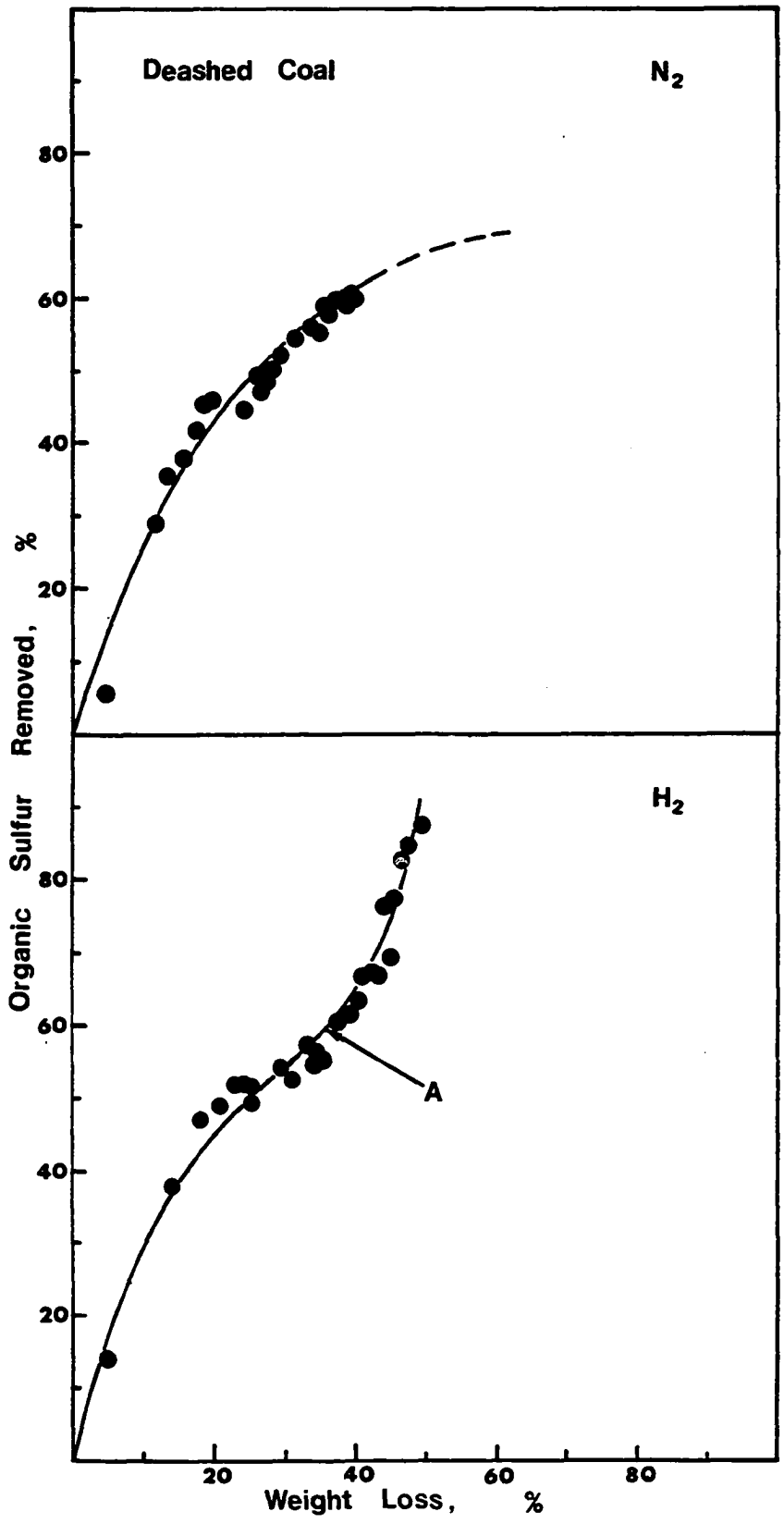
Figure 33. The effect of holding time on the parameters for sulfur reaction scheme with hydrogen treatment at 700 °C


f
.4
.2
G_1
.2
.1
G_2
.9
.8
.7
10
20
30
40
50
60
Time, min

The effectiveness of sulfur removal by direct hydrogenation The effectiveness of sulfur removal by direct hydrogenation can be evaluated by comparing the experimental data from the hydrogen and nitrogen treatments. The sulfur removal in nitrogen atmospheres is due to the release of sulfur compounds as volatile matter during thermal decomposition. A relationship should exist then between the amount of sulfur removed and the volatile matter released. A plot of the organic sulfur removed versus the weight loss for deashed coal heated in nitrogen indeed fell roughly on a smooth line (Figure 34), regardless of the temperature and holding time of the treatment.

In hydrogen, sulfur removal is caused either by devolatilization of sulfur containing material in the coal or by direct hydrogenation of sulfur compounds to form hydrogen sulfide. In general, the amount of sulfur removed is higher in hydrogen than in nitrogen at corresponding temperatures and holding times, and so is the weight loss. In order to evaluate the effectiveness of hydrogenation, a plot of the organic sulfur removed versus the weight loss for deashed coal in hydrogen atmospheres was prepared and is shown also on Figure 34 for comparison. Up to a weight loss of about 40% (point A), the amount of organic sulfur removed in hydrogen at any given weight loss was almost

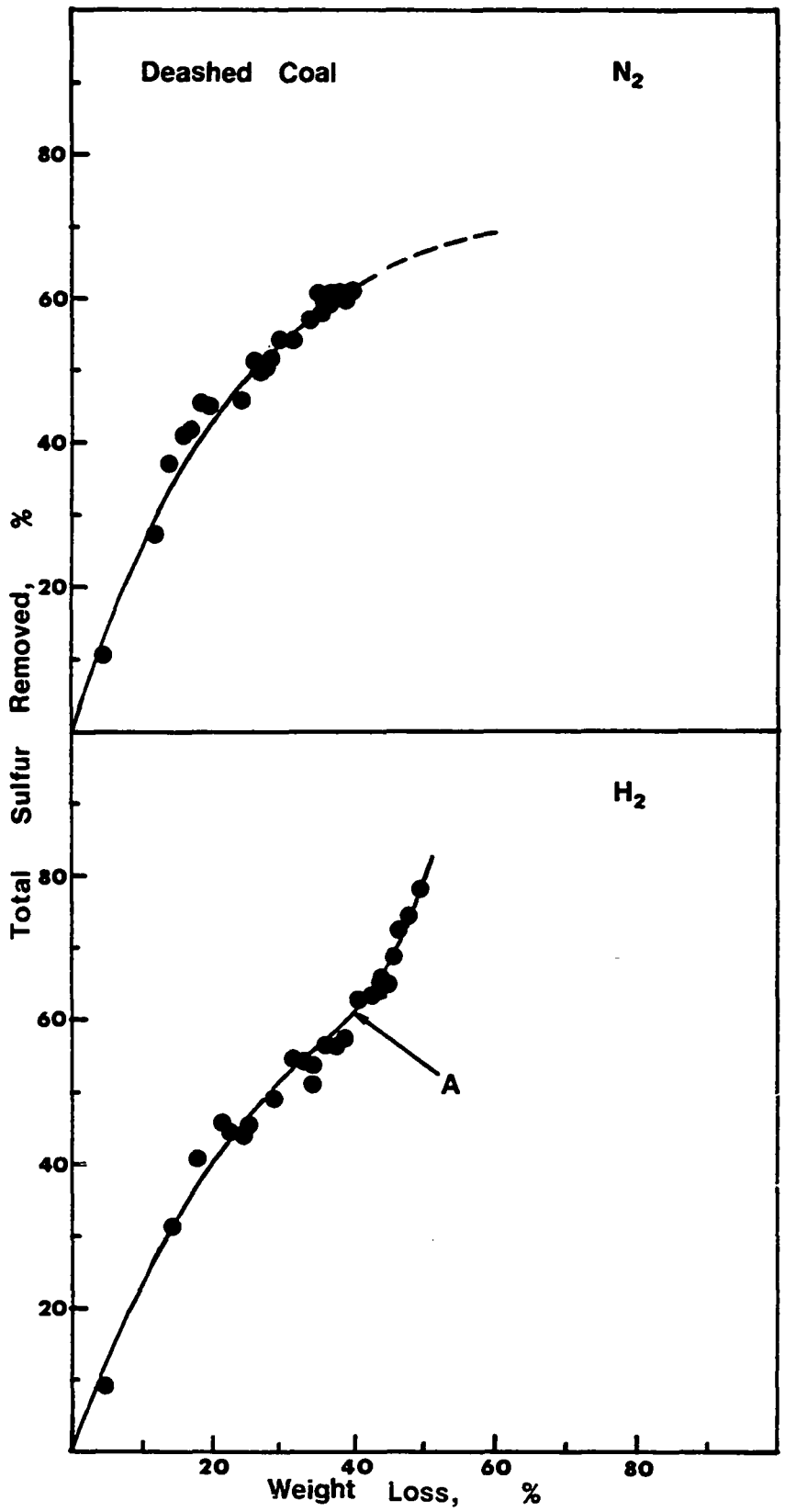
Figure 34. The organic sulfur removed versus weight loss curves for deashed coal in nitrogen and hydrogen atmospheres


Deashed Coal
N_2
H_2
A
Organic Sulfur Removed, %
Weight Loss, %
20
40
60
80

the same as the amount removed in nitrogen. At weight losses greater than 40%, the sulfur removal curves in nitrogen and hydrogen were different. The organic sulfur removal in hydrogen increased rapidly with a slight increase in weight loss. This indicated that direct hydrogenation was taking place. The experimental data in hydrogen above point A were taken at 600 and 700 °C. It appears therefore that direct hydrogenation of the sulfur compounds in coal was only significant at temperatures above 600 °C. At lower temperatures, the apparent higher sulfur reduction in hydrogen when compared to nitrogen was due to the higher weight loss. The same reduction could be achieved in nitrogen at a higher temperature where the weight loss was the same. In actual practice, then, there is no need to use hydrogen during the heating period when the coal is below 600 °C.

Figure 35 shows a plot of the total sulfur removed versus weight loss for deashed coal in both nitrogen and hydrogen atmospheres. The same inflection point (A) was found for the experiments in hydrogen atmospheres above 600 °C. The organic and total sulfur contents of the raw coal did not correlate with weight loss since the raw coal contained a large portion of inorganic sulfur and extensive transformation reactions took place between the various sulfur forms in the sample.

Figure 35. The total sulfur removed versus weight loss curves for deashed coal in nitrogen and hydrogen atmospheres

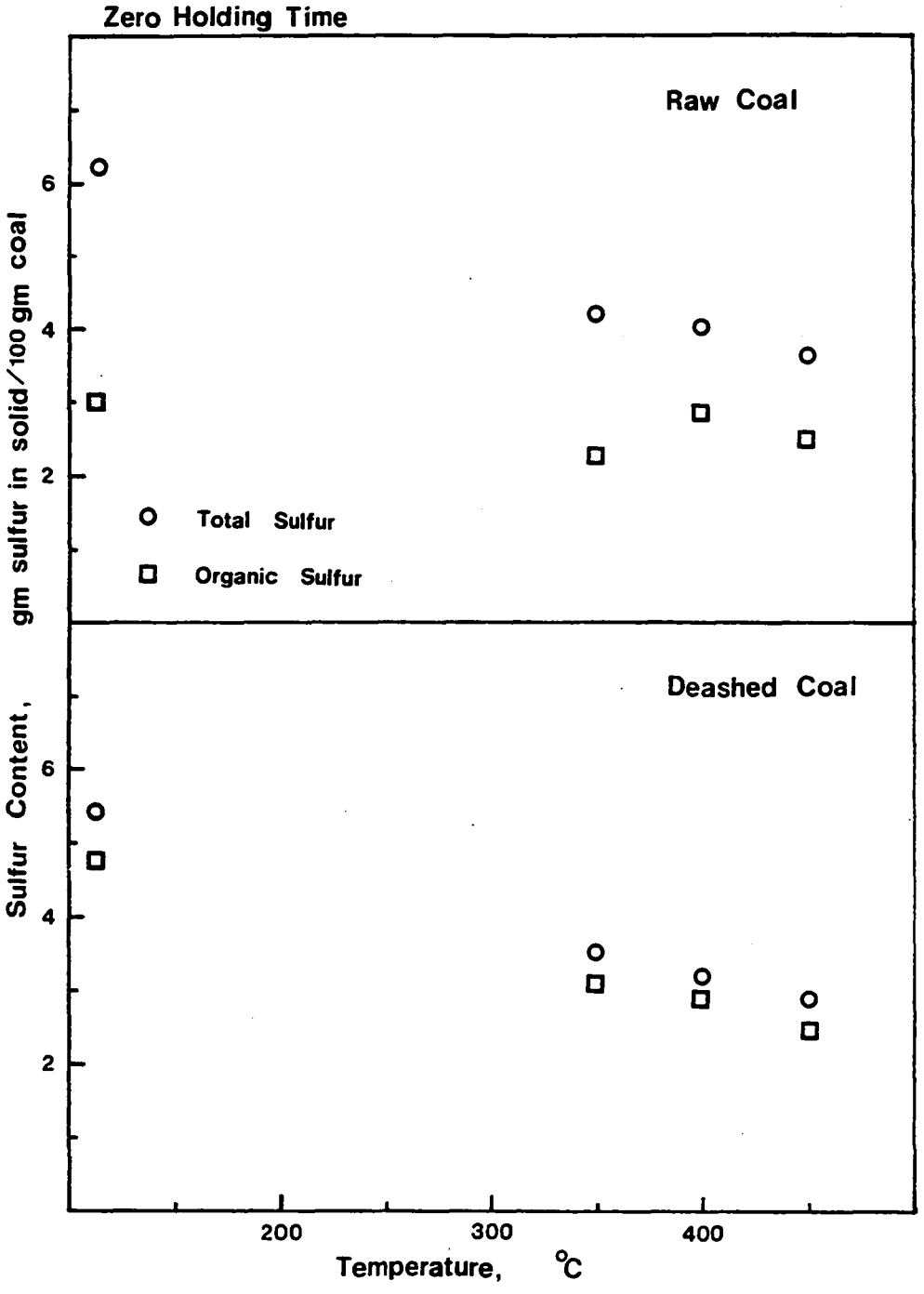

Deashed Coal
N_2
H_2
A
Total Sulfur Removed, %
Weight Loss, %
20
40
60
80

Desulfurization in oxidizing atmospheres

Effect of temperature and holding time A great deal of the coal is oxidized when treated in oxygen containing atmospheres at elevated temperatures. Unlike the gases produced by the evolution of volatile matter in nitrogen or hydrogen, the products of oxidation are mostly carbon dioxide and water which have no heating value. Therefore, the heating value lost by the coal due to oxidation can not be recovered by burning the gases. The extent of oxidation increases with temperature; thus there is an upper limit of temperature beyond which the oxygen treatment is not feasible due to the large weight loss. For Iowa coal this maximum temperature is about 450 °C.

Figure 36 shows the total sulfur and organic sulfur contents of both raw coal and deashed coal as a function of temperature when treated in a 6% oxygen-94% nitrogen gas mixture. The holding time at the final temperature was zero in each case. The total sulfur reduction for both raw coal and deashed coal increased with temperature and was higher than the reduction in both nitrogen and hydrogen atmosphere at the same temperature. However, the weight loss with the oxygen treatment was considerably higher. The excess weight loss with oxygen over that with nitrogen was due to oxidation and was in the range of 4 to 25% based on

Figure 36. The effect of temperature on the total sulfur and organic sulfur contents for both raw coal and deashed coal in oxidizing atmospheres

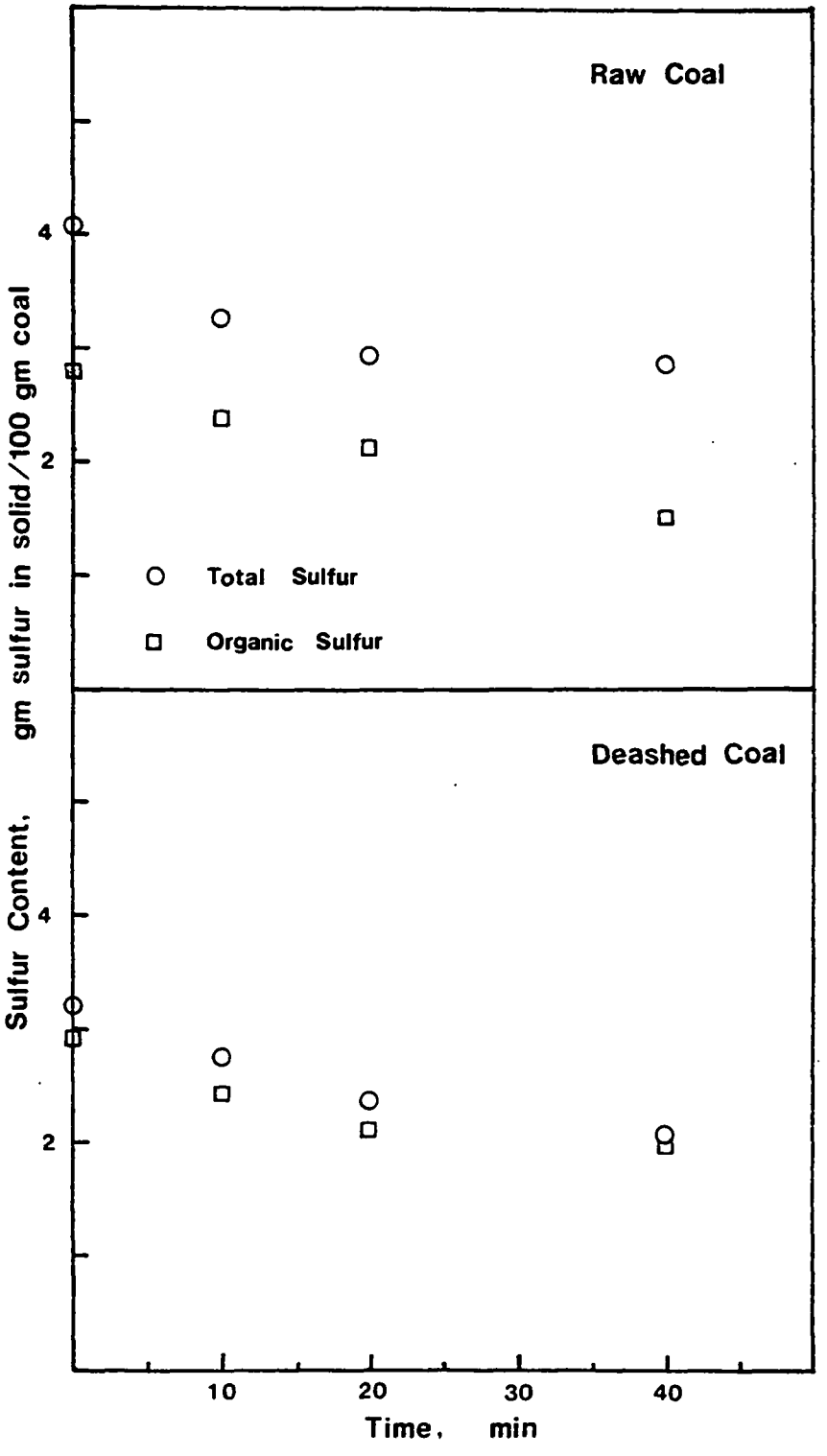

Zero Holding Time
Raw Coal
Deashed Coal
Total Sulfur
Organic Sulfur
gm sulfur in solid/100 gm coal
Sulfur Content,
2
4
6
200
300
400
Temperature, °C

the original weight of the coal sample. It increased rapidly with temperature and holding time. This large weight loss makes oxygen treatment impractical as a method for desulfurization of Iowa coal.

The inorganic sulfur removal in oxidizing atmospheres was higher than in nitrogen and hydrogen at all temperatures studied. This is consistent with thermodynamic studies on the reactions of pyrite since the equilibrium constants for pyrite reactions in oxidizing atmospheres are higher than those in nitrogen (for thermal decomposition) or hydrogen in the range of temperatures studied. The organic sulfur content of deashed coal decreased continuously with temperature, but the organic sulfur content of raw coal first decreased at 350 °C, then increased to a maximum at 400 °C before decreasing again. This indicated that the transformation of inorganic sulfur into organic sulfur also took place in oxidizing atmospheres.

Figure 37 shows the total sulfur and organic sulfur contents of both raw coal and deashed coal at 400 °C as a function of holding time. Unlike the experimental results in nitrogen and hydrogen at this temperature, there was a continuing reduction of organic sulfur up to the largest holding time used, 40 minutes. This was due to oxidation of the whole coal sample which removed sulfur containing material as the carbonaceous material was oxidized since

Figure 37. The effect of holding time on the total sulfur and organic sulfur contents for both raw coal and deashed coal with oxygen treatment at 400 °C


Raw Coal
Deashed Coal
Total Sulfur
Organic Sulfur
Sulfur Content, gm sulfur in solid/100 gm coal
4
2
4
2
10
20
30
40
Time, min

the sulfur reduction was accompanied by a large weight loss.

Transformation of sulfur compounds in oxidizing atmospheres The reaction scheme for the sulfur compounds in coal proposed in the previous section on nitrogen treatment also was applied to interpret the experimental results in oxidizing atmospheres. Figure 38 shows the parameters calculated from the reaction scheme as a function of temperature using the data on Figure 36. The fraction of inorganic sulfur transformed into organic sulfur (f) in oxidizing atmospheres was comparable to that in nitrogen at the same temperature. It increased rapidly from about 0.1 to 0.36 at temperatures between 350 and 450 °C and remained at about 0.36 at 455 °C. The fraction of inorganic sulfur released into the gas phase (G_1) was much larger than in nitrogen or hydrogen. This is because the reaction of pyrite with oxygen is thermodynamically more favorable than the reaction of pyrite with hydrogen. The value of G_1 was almost unchanged with temperature between 350 and 455 °C. The fraction of organic sulfur released into the gas phase (G_2) also was larger than in nitrogen or hydrogen and it increased rapidly with temperature. About 55% of the organic sulfur was released at 455 °C.

Figure 39 shows the parameters calculated from the reaction scheme at 400 °C as a function of holding time by

Figure 38. The effect of temperature on the parameters of sulfur reaction scheme with oxygen treatment

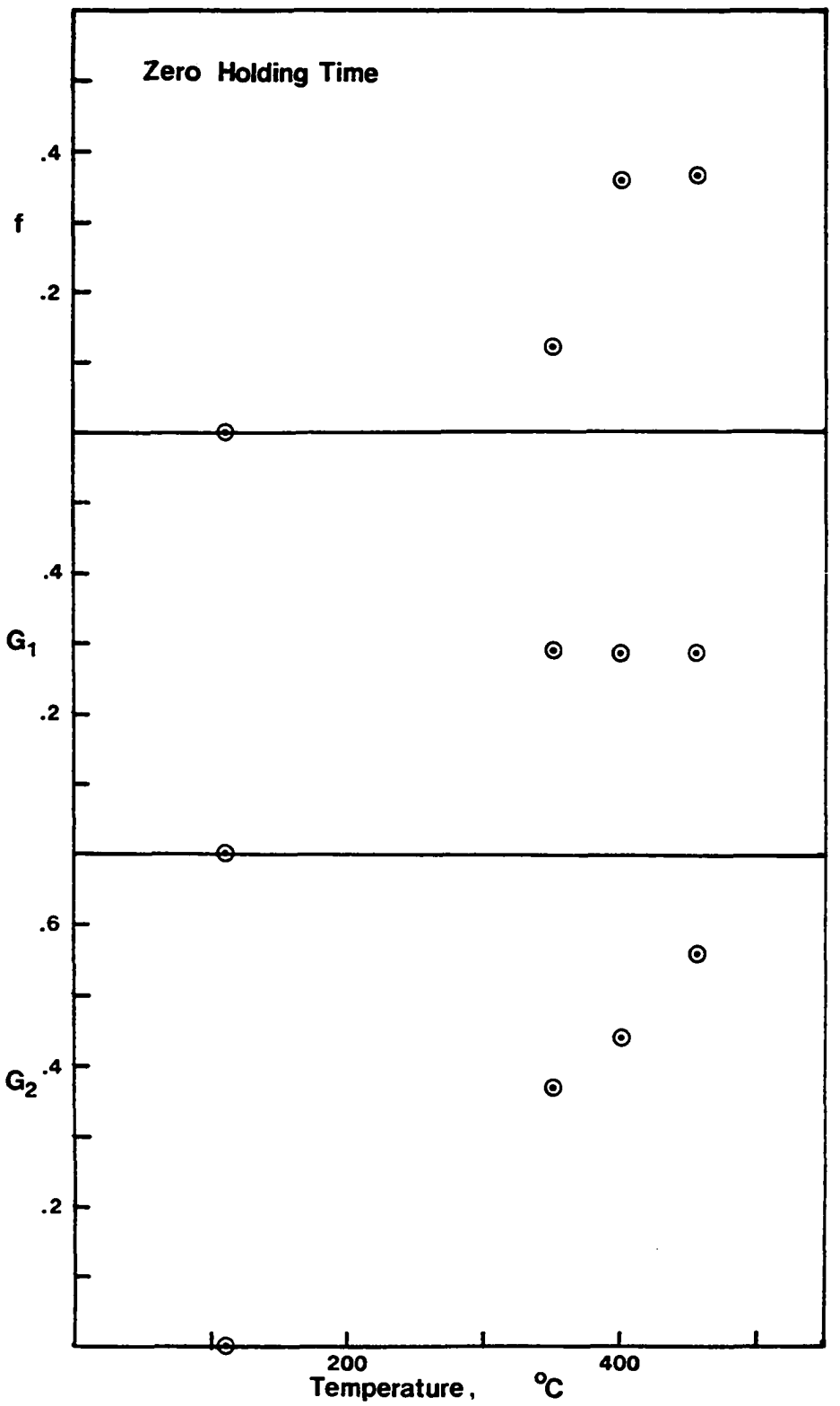
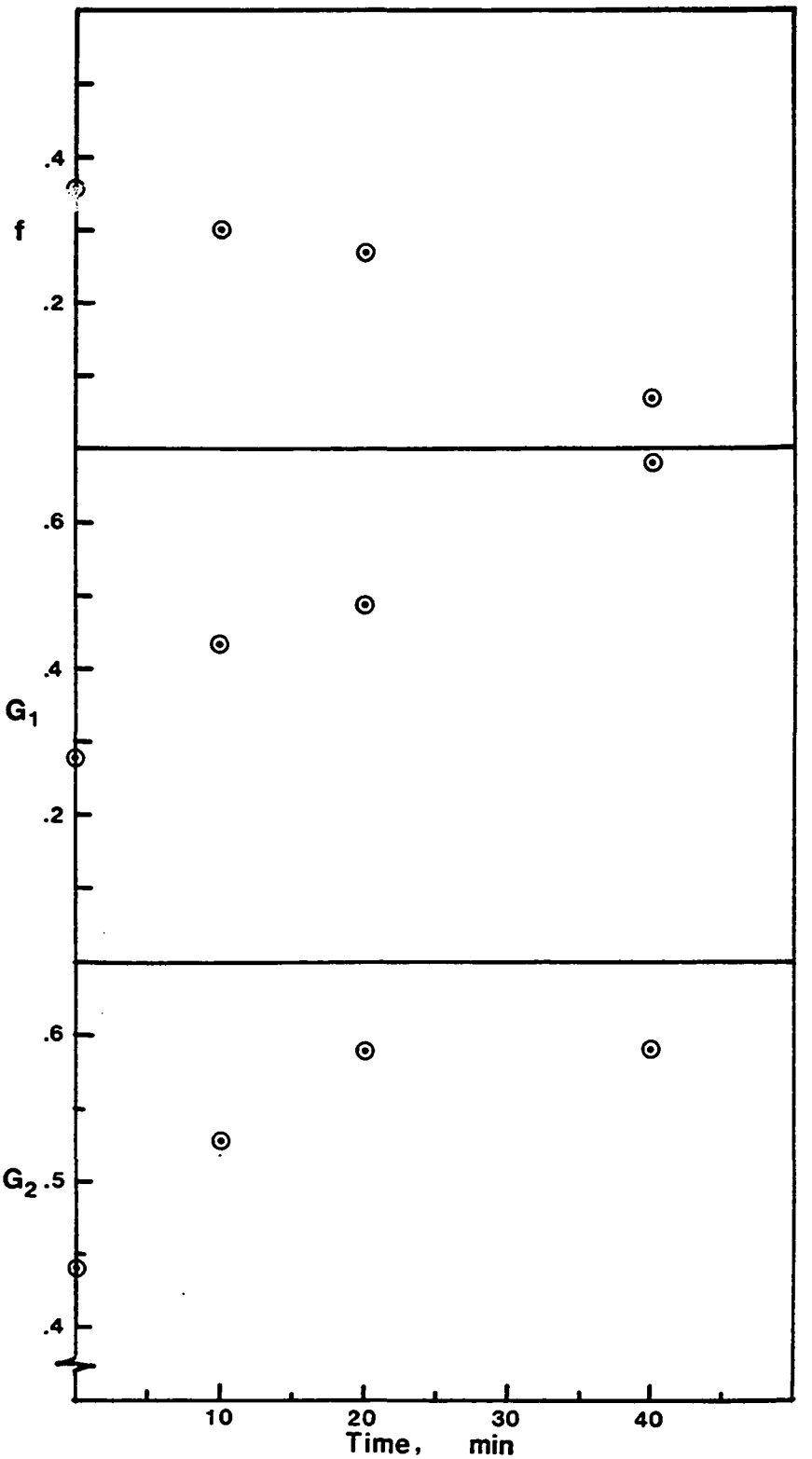

Zero Holding Time
f
.4
.2
G_1
.4
.2
G_2
.6
.4
.2
200
400
Temperature, °C

Figure 39. The effect of holding time on the parameters of sulfur reaction scheme with oxygen treatment at 400 °C


f
.4
.2
G_1
.6
.4
.2
G_2
.6
.5
.4
10
20
30
40
Time, min

using the data on Figure 37. The fraction of inorganic sulfur transformed into organic sulfur decreased with holding time. This indicated that the inorganic sulfur that had previously reacted with the carbonaceous material in the coal was oxidized and released into the gas phase. The fraction of inorganic sulfur released into the gas phase, which was almost unchanged with temperature between 350 and 455 °C, increased rapidly with holding time. The removal of inorganic sulfur in oxidizing atmospheres, therefore, is controlled by the diffusion of oxygen. Since the diffusion of oxygen through the pores in the coal sample is relatively slow, the oxidation of the pyrite requires long treatment times. Also, the rate of diffusion is only slightly dependent upon temperature. The fraction of organic sulfur released into the gas phase increased with holding time. The numerical values of G_2 in oxidizing atmospheres were about 0.1 greater than the values of G_2 in nitrogen at the same treatment conditions. Again, this is attributed to oxidation of the entire coal sample which removed some sulfur containing material as the carbonaceous material was oxidized.

The controlling mechanism of the desulfurization reactions

The desulfurization effect in nitrogen atmospheres has been attributed to the evolution of volatile sulfur compounds, and this devolatilization reaction is controlled

by the rate of chemical reaction. Hydrogenation reactions did not start during the hydrogen treatment below 600 °C. Sulfur removal, therefore, at lower temperatures was still due to devolatilization. An attempt will now be made to find the controlling mechanism for desulfurization after hydrogenation has started, especially for removal of the organic sulfur compounds. The unreacted, shrinking core model of Yagi and Kunii (1955), as modified by Levenspiel (1962) and Wen (1968), is used for analysis of the data. Only those relationships required for the calculations are shown here. The complete mathematical analysis can be found in the original publications.

Wen (1968) showed that for chemical reaction control,

$$t/t^* = 1 - (1-X)^{1/3}$$

For product layer diffusion control,

$$t/t^* = 1 - 3(1-X)^{2/3} + 2(1-X)$$

where X in both cases is the conversion of the reacting material at time t, and t^* is the time required for complete conversion. If $1-(1-X)^{1/3}$ is plotted versus t and $1 - 3(1-X)^{2/3} + 2(1-X)$ versus t, the plot representing the correct controlling mechanism should show a straight line.

Figures 40 and 41 show such plots for the conversion of the organic sulfur in deashed coal using hydrogen at

Figure 40. Determination of the rate controlling mechanism for the desulfurization of deashed coal in hydrogen at 600 °C

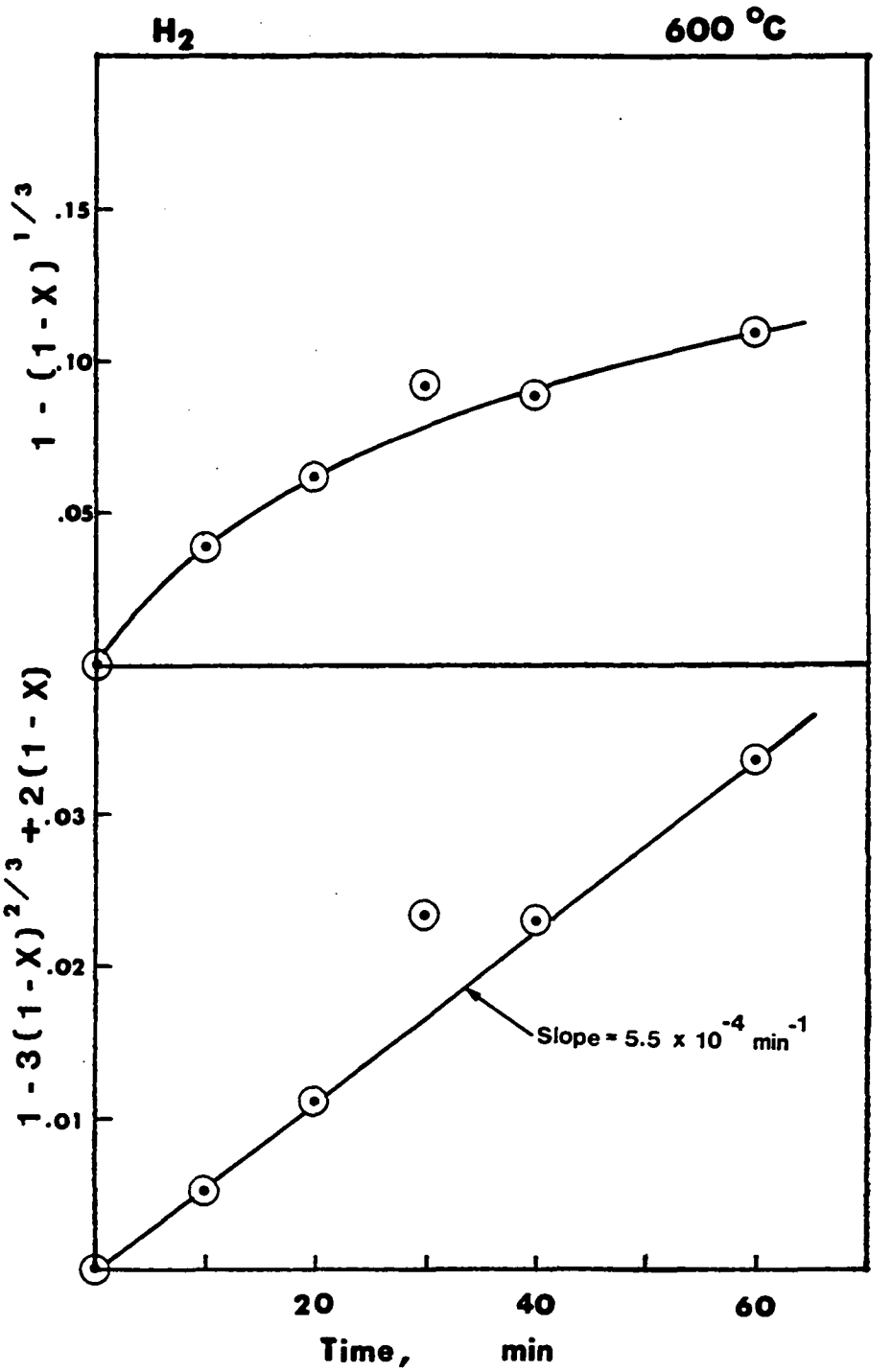
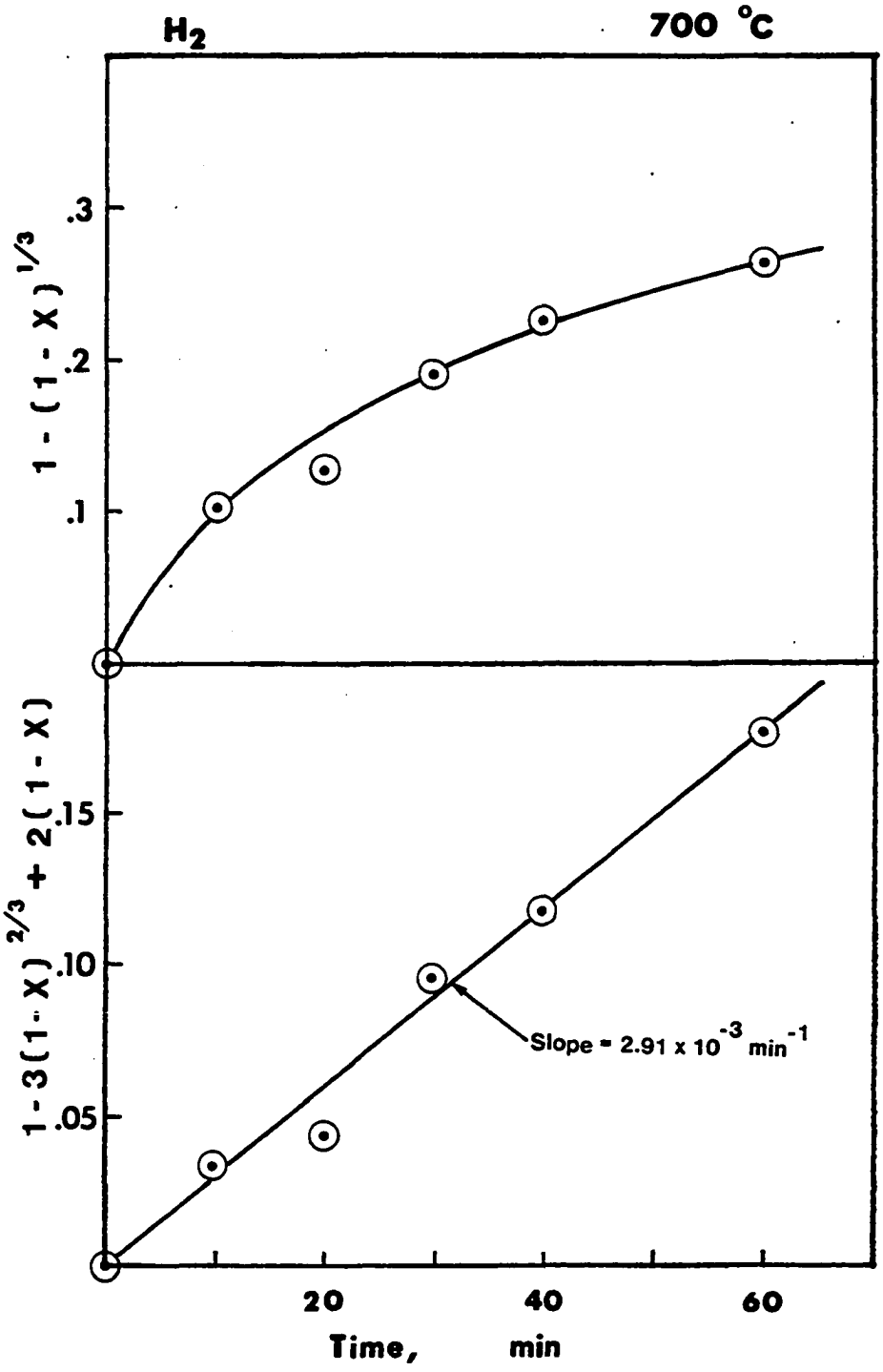

H2
600 °C
1 - (1 - X) 1/3
.15
.10
.05
1 - 3(1 - X) 2/3 + 2(1 - X)
.03
.02
.01
Slope = 5.5 x 10-4 min-1
20
40
60
Time, min

Figure 41. Determination of the rate controlling mechanism for the desulfurization of deashed coal in hydrogen at 700 °C


H2
700 °C
1 - (1 - X)^1/3
.3
.2
.1
1 - 3(1 - X)^2/3 + 2(1 - X)
.15
.10
.05
Slope = 2.91 x 10^-3 min^-1
20
40
60
Time, min

600 and 700 °C, respectively. It appears that product layer diffusion is the controlling mechanism since the plots of $1 - 3(1-X)^{2/3} + 2(1-X)$ versus time are linear at both temperatures.

The slope of the $1 - 3(1-X)^{2/3} + 2(1-X)$ versus t plot equals $1/t^*$, which is proportional to the effective diffusivity of the reacting gas in the solid pore. As shown in Figures 40 and 41, there is a five-fold difference in the slope between 600 and 700 °C. The change of molecular diffusivity with temperature could hardly account for this large increase. It is most likely that the coal particles undergo some structural change and the microporosity increases in this temperature range. Evans and Hermann (1970) reported that during the carbonization of low rank Yallourn coal (27% oxygen), a new set of pores was opened due to the detachment of molecular fragments. The increase in microporosity between 400 and 700 °C was 0.30 cm^3/cm^3, independent of the macro-structure of the coal. This report supports the large increase in effective diffusivity with temperature found in this research. From the extrapolation of the slopes in Figures 40 and 41, the times required for complete conversion of the organic sulfur compounds at 600 and 700 °C are 28 hours and 55 hours, respectively.

From Figures 38 and 39, the fraction of inorganic sulfur

released as gases in oxidizing atmospheres was almost unchanged with temperature between 350 and 455 °C. However, it increased rapidly with holding time at 400 °C. This indicated that the removal of inorganic sulfur in oxidizing atmosphere was controlled by the diffusion of oxygen at the treatment conditions. Since the diffusion of oxygen through the pores in the coal sample is relatively slow and the oxidation of the pyrite requires long treatment time. Also, the rate of diffusion is only slightly dependent upon temperature.

Summary and Comments

The desulfurization of Iowa coal in nitrogen, hydrogen and a 6% oxygen-94% nitrogen gas mixture was studied. Two samples of an Iowa coal from the Jude mine were used in the experiments, the raw coal and a deashed Jude coal. The raw coal contained about 6.3% sulfur, half organic and half inorganic, while the deashed coal contained 5.4% sulfur, mostly organic. The effect of temperature and holding time were investigated at different conditions. In general, the amount of sulfur removed increased with both temperature and holding time. It also was affected by the gas used, and increased with gas type in the order nitrogen, hydrogen and the oxygen-nitrogen mixture. However, the weight loss of the sample during the treatment also was the greatest in the

oxygen containing mixture.

It was observed in the experiments that some inorganic sulfur was transformed into organic sulfur during the treatment. A reaction scheme for the sulfur compounds in coal which accounted for this observation was proposed. Using this scheme, the fraction of inorganic sulfur transformed into organic sulfur and the fractions of organic and inorganic sulfur released as gases were calculated for the different treatment conditions. In general, these fractions increased with temperature in either nitrogen, hydrogen or oxidizing atmospheres. However, the influence of holding time on these fractions depended on the gas type and temperature. The fraction of inorganic sulfur transformed into organic sulfur increased with holding time in nitrogen and hydrogen at low temperatures, but it decreased with holding time in oxygen and hydrogen at high temperatures. The fraction of inorganic sulfur released as a gas in nitrogen or hydrogen showed little dependence on holding time, but increased rapidly with holding time in oxidizing atmospheres. The fraction of organic sulfur released as a gas increased with holding time for all gas types and temperatures studied.

The rate controlling mechanism for desulfurization in nitrogen was found to be the rate of chemical reaction. The desulfurization in hydrogen also was controlled by the

rate of chemical reaction at temperatures below 500 °C. Direct hydrogenation of the sulfur compounds in coal took place at temperatures above 600 °C and the rate controlling step became the rate of diffusion of hydrogen through the product layer. The rate of removal of inorganic sulfur in oxidizing atmosphere was controlled by the diffusion of oxygen through the pores in the coal sample.

The extent of desulfurization at a given treatment condition depends strongly on the coal type. It was shown in the study by Černič-Simić (1962) that the portion of organic sulfur released during carbonization increased as the rank of the coal sample decreased. On the other hand, the fixation of the inorganic sulfur by the carbonaceous material in the coal also increased as the rank of the coal decreased. The differences in ash content of different coal samples also has some influence on desulfurization, since the coal ash retains sulfur when heated to high temperatures. Therefore, gas treatment may be more attractive with certain types of coal.

In any case, it is easier to desulfurize the organic portion of the coal sample alone rather than the total sample when using gases at elevated temperatures. The success of this treatment, then, depends on an effective physical separation process to eliminate most of the

inorganic sulfur and ash and on an economical gas cleaning process to remove the sulfur compounds in the gas phase so its heating value may be utilized. This is particularly true for coals with large inorganic sulfur and ash contents and coals of lower ranks.

Sulfur removal from Iowa coal during treatment with nitrogen is not adequate. Sulfur removal in oxygen is high but a large quantity of the potential heating value is lost through oxidation. Therefore, it is not feasible to use oxygen for desulfurization of Iowa coal. The most attractive desulfurization process utilizing gas treatment appears to be one that begins with a physical separation step to remove most of the inorganic sulfur and ash. Some advanced physical separation process such as froth flotation or oil agglomeration might be used. This would be followed by treatment in hydrogen at 700 °C. The hydrogen consumption could be minimized by heating the coal in an inert atmosphere to 700 °C since hydrogasification does not take place during the heating period. The gas produced would be cleaned and utilized as a fuel gas.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Devolatilization

1. The ultimate volatile matter released at a given temperature is a function of temperature only under the experimental conditions of this study. It is independent of the particle size, the heating rate and the path followed in heating the coal to the final temperature.
2. The devolatilization reaction at a constant temperature condition shows three reaction stages; an initial rapid reaction stage is followed by a longer, intermediate stage with a slower rate of weight loss, with the final step having a very small and almost constant rate of weight loss.
3. The rate of devolatilization in both the rapid reaction stage and the intermediate stage can be represented by first order reaction kinetics and there is an effective first order reaction rate constant for each reaction stage. The effective rate constants for each stage obtained at different temperatures are roughly linear on an Arrhenius plot and the effective activation energy for each reaction stage is about 1.2 Kcal/mole.

4. A model was proposed to predict the weight loss during constant-rate heating by using the ultimate weight loss at different temperatures and the reaction rate constants obtained in the constant temperature experiments. The model agrees well with the weight losses observed in the experiments for different heating rates.

Desulfurization

1. Temperature is the most important factor influencing desulfurization in nitrogen and hydrogen, as well as in oxidizing atmospheres. The holding time at the final temperature is less important with nitrogen or hydrogen treatments at temperatures below 500 °C, but has some effect with oxygen treatment and hydrogen treatment at temperatures above 600 °C. Hydrogen treatment is more effective in the removal of organic sulfur, while oxygen is more effective in removing inorganic sulfur.
2. It was observed in the experiments that some inorganic sulfur was transformed into organic sulfur during the treatment in either nitrogen, hydrogen or oxidizing atmospheres. A reaction scheme for sulfur compounds in coal was proposed to interpret the experimental results. The fraction of inorganic

sulfur transformed into organic sulfur, the fraction of inorganic sulfur released as gases, and the fraction of organic sulfur released as gases were calculated for each gas atmosphere at the different treatment conditions.

3. Desulfurization in nitrogen is controlled by the rate of the chemical reaction. The desulfurization in hydrogen atmospheres also is chemical reaction rate controlled at temperatures below 500 °C. Direct hydrogenation of the sulfur compounds in the coal takes place at temperatures above 600 °C and the rate controlling step shifts to the diffusion of hydrogen through the product layer. The removal of inorganic sulfur in oxidizing atmospheres is controlled by the diffusion of oxygen through the pores in the sample.

Recommendations

1. A better understanding of the basic structure of coal and its physical and chemical changes is of major importance to the study of devolatilization and desulfurization of coal. To apply the reaction model to industrial processes where heat and mass transfer have some effect on the reaction or to suggest certain treatments and reactor designs to

alleviate these physical limitations requires a thorough knowledge of coal at the treatment conditions. Future studies in this direction are recommended.

2. Both devolatilization and desulfurization depend strongly on the type of coal studied. It is of interest to investigate these reactions for a wide range of coal samples and to correlate the reaction parameters with the standard properties of the coal sample such as coal rank, volatile matter content, ash content, or organic and inorganic sulfur contents.

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APPENDIX A: MATHEMATICAL PROPERTIES OF THE SOLUTION OF THE WEIGHT LOSS MODEL

$$\frac{V}{V_0} = 1 - \frac{\int_{T=T_0}^{T=T} e^{\int^{T} \frac{k(T)}{m}} dV_0}{e^{\int^{T} \frac{k(T)}{m}\, dT}\, V_0}$$

i) $0 \leq \frac{V}{V_0} \leq 1.$

Both V_0 and $k(T)$ are positive monotone increasing with respect to T. So $e^{\int^{T} \frac{k(T)}{m}\, dT}$ is monotone increasing with respect to T and also to V_0 (m is positive).

$$0 \leq \frac{\int_{T=T_0}^{T=T} e^{\int^{T} \frac{k(T)}{m}\, dT} dV_0}{e^{\int^{T} \frac{k(T)}{m}\, dT}\, V_0} \leq 1$$

Thus $0 \leq \frac{V}{V_0} \leq 1$

ii) $(\frac{\partial V}{\partial m})_T < 0.$

$$(\frac{\partial V}{\partial m})_T = \frac{\int_{T=T_0}^{T=T} (\int^T \frac{k(T)}{m} dT) e^{\int^T \frac{k(T)}{m} dT} dV_0 - \int^T \frac{k(T)}{m} dT \int_{T=T_0}^{T=T} e^{\int^T \frac{k(T)}{m} dT} dV_0}{e^{\int^T \frac{k(T)}{m} dT}}$$

Since both $\int^T \frac{k(T)}{m^2} dT$ and $e^{\int^T \frac{k(T)}{m} dT}$ are positive increasing functions with respect to V_0.

$$\int_{T=T_0}^{T=T} (\int^T \frac{k(T)}{m^2} dT) e^{\int^T \frac{k(T)}{m} dT} dV_0$$

$$< \int^T \frac{k(T)}{m^2} dT \int_{T=T_0}^{T=T} e^{\int^T \frac{k(T)}{m} dT} dV_0$$

Thus $(\frac{\partial V}{\partial m})_T < 0$

iii) $\lim_{m \to \infty} \frac{V}{V_0} = 0.$

$$\lim_{m \to \infty} \frac{V}{V_0} = 1 - \frac{\int_{T=T_0}^{T=T} dV_0}{V_0} = 0$$

iv) $\lim_{m\to 0} \frac{V}{V_0} = 1.$

$$\int_{T=T_0}^{T=T} e^{\int^{T} \frac{k(T)}{m}\, dT}\, dV_0 = e^{\int^{T'} \frac{k(T)}{m}\, dT} V_0$$

where $T_0 < T' < T$.

$$\frac{\int_{T=T_0}^{T=T} e^{\int^{T} \frac{k(T)}{m}\, dT}\, dV_0}{e^{\int^{T} \frac{k(T)}{m}\, dT} V_0} = \left(\frac{e^{\int^{T'} k(T)dT}}{e^{\int^{T} k(T)dT}}\right)^{\frac{1}{m}}$$

$e^{\int^{T} k(T)dT}$ is positive increasing function of T. So

$$0 < \frac{e^{\int^{T'} k(T)dT}}{e^{\int^{T} k(T)dT}} < 1$$

$$\lim_{m\to 0} \frac{V}{V_0} = 1 - \left(\frac{e^{\int^{T'} k(T)dT}}{e^{\int^{T} k(T)dT}}\right)^{\frac{1}{m}}$$

$$= 1-0$$

$$= 1.$$

APPENDIX B: EXPERIMENTAL DATA FOR DESULFURIZATION

Table B1. Raw coal (total sulfur 6.29%, organic sulfur 3.04%) in nitrogen

Temp. (°C)	Holding time (minute)	Total sulfur content (gm S/100 gm coal)	Organic sulfur content (gm S/100 gm coal)	Weight recovery (%)
300	0	5.98	2.92	96.7
400	0	5.21	2.51	88.9
400	5	5.03	2.42	87.3
400	10	4.75	2.32	86.4
400	15	4.87	2.30	85.7
400	20	4.80	2.32	85.2
400	40	4.82	2.27	83.9
500	0	4.70	2.71	79.6
500	5	4.75	-	78.2
500	10	4.68	-	77.5
500	15	4.65	3.49	76.8
500	20	4.54	-	76.5
500	40	4.63	2.77	75.5
600	0	4.41	2.82	74.0
600	5	4.39	3.21	72.5
600	10	4.32	-	71.3
600	15	4.13	-	70.5
600	20	4.08	2.74	69.9
600	40	4.12	3.13	68.3
700	0	3.81	3.28	68.0
700	5	3.90	3.42	65.8
700	10	3.71	3.46	64.8
700	15	3.98	-	63.7
700	20	3.91	3.21	62.7
700	40	3.79	3.29	60.8

Table B2. Deashed coal (total sulfur 5.43%, organic sulfur 4.74%) in nitrogen

Temp. (°C)	Holding time (minute)	Total sulphur content (gm S/100 gm coal)	Organic sulfur content (gm S/100 gm coal)	Weight recovery (%)
300	0	4.86	4.50	95.3
400	0	3.95	3.40	88.1
400	5	3.41	3.08	86.0
400	10	3.22	2.96	83.9
400	15	3.17	2.77	82.5
400	20	2.97	2.59	81.5
400	40	3.04	2.57	80.2
500	0	2.98	2.65	75.1
500	5	2.65	2.43	73.9
500	10	2.72	2.54	72.9
500	15	2.69	2.47	72.0
500	20	2.64	2.40	71.5
500	40	2.50	2.30	70.4
600	0	2.52	2.18	68.4
600	5	2.33	2.14	65.7
600	10	2.29	2.17	64.4
600	15	2.18	2.01	63.7
600	20	2.20	1.98	63.0
600	40	2.15	1.94	62.9
700	0	2.11	1.97	64.5
700	5	2.16	1.95	63.2
700	10	2.16	1.97	62.4
700	15	2.15	2.02	61.6
700	20	2.18	1.95	60.9
700	40	2.15	1.95	59.8

Table B3. Raw coal (total sulfur 6.29%, organic sulfur 3.04%) in hydrogen

Temp. (°C)	Holding time (minute)	Total sulfur content (gm S/100 gm coal)	Organic sulfur content (gm S/100 gm coal)	Weight recovery (%)
300	0	6.03	2.92	95.8
400	0	5.23	2.72	88.5
400	10	4.94	2.57	85.5
400	20	4.80	2.70	83.6
400	30	4.78	2.56	82.1
400	40	4.70	2.66	81.2
400	60	4.84	2.75	80.5
500	0	4.52	2.98	78.0
500	10	4.08	2.86	75.0
500	20	3.79	2.68	73.1
500	30	3.92	2.40	72.4
500	40	3.73	2.41	71.8
500	60	3.72	2.33	71.4
600	0	3.79	2.72	71.0
600	10	3.50	2.53	68.8
600	20	3.46	2.59	68.0
600	30	3.23	2.60	67.3
600	40	3.47	2.40	66.8
600	60	3.08	2.34	66.5
700	0	3.54	2.38	67.3
700	10	3.03	2.07	64.8
700	20	2.81	1.89	63.5
700	30	2.83	1.42	62.5
700	40	2.70	1.19	61.7
700	60	2.31	1.04	61.0

Table B4. Deashed coal (total sulfur 5.43%, organic sulfur 4.74%) in hydrogen

Temp. (°C)	Holding time (minute)	Total sulfur content (gm S/100 gm coal)	Organic sulfur content (gm S/100 gm coal)	Weight recovery (%)
300	0	4.93	4.09	95.0
400	0	3.75	2.96	85.9
400	10	3.23	2.52	82.0
400	20	2.96	2.42	79.0
400	30	3.03	2.30	77.0
400	40	3.05	2.29	75.8
400	60	3.00	2.30	75.0
500	60	3.13	2.41	74.6
500	10	2.81	2.20	70.4
500	20	2.47	2.28	68.5
500	30	2.48	2.05	66.8
500	40	2.69	2.26	65.3
500	60	2.39	2.16	63.6
600	0	2.53	2.11	65.4
600	10	2.37	1.85	61.2
600	20	2.07	1.74	59.1
600	30	2.07	1.57	57.6
600	40	2.00	1.59	56.5
600	60	1.97	1.49	55.0
700	0	2.08	1.57	58.8
700	10	1.87	1.15	56.2
700	20	1.72	1.07	54.5
700	30	1.52	0.83	53.4
700	40	1.42	0.74	52.4
700	60	1.23	0.62	50.6

Table B5. Raw coal (total sulfur 6.29%, organic sulfur 3.04%) in oxygen-nitrogen mixture

Temp. (°C)	Holding time (minute)	Total sulfur content (gm S/100 gm coal)	Organic sulfur content (gm S/100 gm coal)	Weight recovery (%)
350	0	4.23	2.29	88.6
350	20	3.34	2.21	80.1
350	40	3.18	2.06	75.2
400	0	4.05	2.85	84.6
400	10	3.29	2.41	78.0
400	20	2.95	2.11	72.6
400	40	2.86	1.46	66.3
455	0	3.68	2.51	79.0
455	20	2.82	2.31	64.1
455	40	2.33	1.86	56.5

Table B6. Deashed coal (total sulfur 5.43%, organic sulfur 4.74%) in oxygen-nitrogen mixture

Temp. (°C)	Holding time (minute)	Total sulfur content (gm S/100 gm coal)	Organic sulfur content (gm S/100 gm coal)	Weight recovery (%)
350	0	3.48	3.05	90.0
350	20	3.09	2.71	82.5
350	40	2.81	2.68	78.2
400	0	3.16	2.88	85.2
400	10	2.72	2.44	77.8
400	20	2.40	2.11	71.6
400	40	2.02	1.99	64.3
455	0	2.98	2.33	77.6
455	20	2.44	2.11	62.5
455	40	1.58	1.51	53.1

APPENDIX C: THE CALCULATED PARAMETERS FOR SULFUR REACTION AND A SAMPLE CALCULATION

Table C1. Nitrogen atmosphere

Temp. (°C)	Holding time (minute)	f from Eq. (1)	G_1 from Eq. (2)	G_2 from Eq. (3)	G_2 from Eq. (4)
300	0	0.01	0.05	0.06	0.07
400	0	0.12	0.08	0.30	0.30
400	5	0.16	0.10	0.37	0.37
400	10	0.15	0.17	0.40	0.39
400	15	0.19	0.06	0.44	0.44
400	20	0.23	0.05	0.48	0.49
500	0	0.36	0.05	0.49	0.49
600	0	0.50	0.01	0.61	0.61
700	0	0.71	0.13	0.69	0.[illegible]
700	5	0.75	0.09	0.70	0.70
700	10	0.76	0.12	0.70	0.70
700	20	0.70	0.09	0.69	0.69
700	40	0.72	0.13	0.69	0.69

Table C2. Hydrogen atmosphere

Temp. (°C)	Holding time (minute)	f from Eq. (1)	G_1 from Eq. (2)	G_2 from Eq. (3)	G_2 from Eq. (4)
300	0	0.10	-0.05	0.15	0.15
400	0	0.29	-0.06	0.42	0.42
400	10	0.34	-0.06	0.52	0.52
400	20	0.41	-0.05	0.55	0.55
400	30	0.38	-0.07	0.57	0.57
400	40	0.42	-0.05	0.58	0.58
400	60	0.45	-0.08	0.58	0.58
500	0	0.51	0.02	0.58	0.59
500	10	0.51	0.02	0.61	0.61
500	20	0.43	0.22	0.58	0.58
500	30	0.39	0.12	0.62	0.62
500	40	0.34	0.20	0.57	0.57
500	60	0.34	0.23	0.59	0.59
600	0	0.49	0.13	0.62	0.63
600	10	0.48	0.14	0.68	0.68
600	20	0.52	0.19	0.71	0.71
600	30	0.57	0.15	0.75	0.75
600	40	0.49	0.14	0.73	0.74
600	60	0.49	0.o9	0.76	0.76
700	0	0.49	0.09	0.74	0.74
700	10	0.47	0.10	0.83	0.83
700	20	0.43	0.17	0.84	0.84
700	30	0.32	0.15	0.87	0.87
700	40	0.25	0.19	0.88	0.88
700	60	0.23	0.29	0.90	0.90

Table C3. Oxygen-nitrogen gas mixture

Temp. (°C)	Holding time (minute)	f from Eq. (1)	G_1 from Eq. (2)	G_2 from Eq. (3)	G_2 from Eq. (4)
350	0	0.12	0.29	0.37	0.37
350	20	0.17	0.49	0.45	0.45
350	40	0.12	0.54	0.45	0.45
400	0	0.36	0.28	0.44	0.44
400	10	0.30	0.43	0.53	0.53
400	20	0.27	0.48	0.59	0.59
400	40	0.07	0.68	0.59	0.59
455	0	0.36	0.28	0.56	0.56
455	20	0.34	0.50	0.60	0.60
455	40	0.32	0.54	0.73	0.73

Sample calculation:

From sulfur contents of original coal samples,

$$S_i^* = 3.25, \quad S_o^* = 3.04$$

$$\alpha S_i^* = 0.69, \quad \beta S_o^* = 4.74$$

$$\alpha = 0.212 \qquad \beta = 1.559$$

With oxygen treatment at 455 °C for 40 minutes (from table, Appendix B),

$$S_o = 1.86, \quad S_i = 0.47$$

$$S_o' = 1.51, \quad S_i' = 0.07$$

from Eq. (1)

$$f = \frac{1.559S_o - S_o'}{(1.559-0.212)x3.25} = 0.32$$

from Eq. (2)

$$G_1 = 1 - f - \frac{S_i}{3.25} = 0.54$$

from Eq. (3)

$$G_2 = 1 - \frac{S_o}{3.04} + \frac{3.25}{3.04} f = 0.73$$

from Eq. (4)

$$G_2 = 1 - \frac{S_o'}{4.74} + \frac{0.69}{4.74} f = 0.73$$